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Author(s)	HORIUTI, Juro
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# CATALYTIC MECHANISM OF THE HYDROGEN ELECTRODE PROCESS AND THE THEORY OF REACTION RATE

By

JURO HORIUTI

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## Introduction

It is well known since TAFEL<sup>1)</sup> that the logarithm of the cathodic current density  $i_c$  of the hydrogen electrode varies linearly with the overpotential  $-\eta$  of the electrode with an inclination<sup>1)</sup>,

$$\alpha \equiv -\frac{RT}{F} \frac{\partial \log i_c}{\partial \eta} \quad (\text{I})$$

lying near 0.5 in most of cases, where  $F$  is Faraday,  $R$  the gas constant and  $T$  absolute temperature. The inclination  $\alpha$  is, however, derived theoretically at 2 instead by the same author<sup>1)</sup> essentially from the relations,

$$a^H \propto \theta \quad (\text{II. a})$$

$$i_c \propto \theta^2 \quad (\text{II. b})$$

based on the simple mass action law applied to the rate-determining step,



of the catalytic mechanism, where  $\theta$  is the fraction of the electrode surface covered by adsorbed hydrogen atoms  $\text{H(a)}$  and  $a^H$  their activity.

This discrepancy has long been taken a strong disproof against the catalytic mechanism, notwithstanding the important question raised by HABER and RUSS<sup>2)</sup> on the validity of the mass action law to the hydrogen atoms on the surface at that time of TAFEL<sup>1)</sup> as well as the striking parallelism between hydrogen overpotential and the catalytic activity for the recombination of the hydrogen atoms discovered by BONHOEFFER<sup>3)</sup>.

OKAMOTO, HORIUTI and HIROTA<sup>4)</sup> (abbreviated to OHH in what follows) invalidated this disproof by deriving  $\alpha \doteq 0.5$  from the catalytic mechanism, resorting to generalization of the statistical mechanical theory of reaction rate taking the repulsive interaction between adsorbed hydrogen atoms into account, which brings about identically the implication of the activity coefficient  $f^*$  of the activated complex in the rate expression of the heterogeneous reaction invariably as in the BRÖRSTED'S theory<sup>5)</sup> of homogeneous reaction, the formulation of the kinetic law deviating from the simple mass action law as foreshadowed by HABER and RUSS<sup>2)</sup>, and the confirmation of the BONHOEFFER series of overpotential referred to above<sup>3)</sup>.

EYRING, GLASSTONE and LAIDLER<sup>6)</sup> (abbreviated to GLE) have later used (II)<sup>\*)</sup> again concluding  $\alpha=2$  against the catalytic mechanism as done by TAFEL; they have stated (II) as valid only at small  $\theta$  without, however, examining practically the validity of the latter condition in the very state of the hydrogen electrode where  $\alpha \doteq 0.5$  is observed.

HICKLING and SALT<sup>8)</sup> replaced  $\alpha^H \propto \theta^{1/n}$  for (II. a) in accordance with the Freundlich's empirical relation while reserving (II. b), where  $n$  is the well-known FREUNDLICH'S constant ranging from 1 to 5, thus arriving at a qualitative explanation of the TAFEL'S relation.

GLE<sup>6)</sup> warn, however, in a footnote<sup>\*\*)</sup> with special reference to the electrode process that the product  $k_v \alpha^I$  of the rate constant  $k_v$  and the activity product  $\alpha^I$  of the initial complex  $I$  of the elementary reaction in question does not give its rate  $\bar{v}$  exactly as

$$\bar{v} = k_v \alpha^I \quad (\text{IV})$$

but the result should be divided by  $f^*$  as

$$\bar{v} = k_v \alpha^I / f^* \quad (\text{V})$$

This statement is literally correct and formally in concordance with the previous work<sup>4)</sup> of OHH, although not itself of much content, since  $f^*$  is not explicitly given nor actually allowed for by GLE; if they did at all and inferred consistently with their view of admitting the repulsive interactions among adsorbed hydrogen atoms<sup>\*\*\*)</sup>, they would have arrived at the same conclusion as that of OHH<sup>4)</sup> rather than that

\*) (II) refers to (II.a) and (II.b) together; this manner of reference will be followed whole throughout the present paper.

\*\*) foot-note † on page 576 of Ref. (7).

\*\*\*) Ref. (7), pp. 359-369.

from the simple mass action law.

Recent followers of GLE seem completely to ignore the above warning of them without any care of  $f^*$  modulating the rate. They take customarily the electrostatical interactions between the activated complex and the surroundings into account in terms of "the electrochemical standard activation free energy" but one-sidedly not the non-electrostatic part of the interaction e. g. the quantum-mechanical exchange repulsions along with the negligence of the  $1/f^*$ -factor<sup>9)</sup>.

They write  $k_v$  of (IV) as,

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

for steps of the activated complex with energy not affected by the electric field as in the case of the catalytic mechanism, where  $\kappa$  is the transmission coefficient,  $k$  the BOLTZMANN's constant,  $h$  the PLANCK's constant and  $\Delta G_0$  the standard activation free energy, but they hardly come at the "absolute rate" because of the vague conception of  $\Delta G_0$ <sup>10)</sup> in the case of the heterogeneous reaction, as exemplified by a mistake demonstrated in §7 of this paper.

These weak points of the followers i. e. negligence of  $f^*$  and the lack of a clear conception of  $\Delta G_0$  are however, more or less inherent to the application of the method of GLE to heterogeneous reactions, it being essentially the extension by analogy of the transition state method put forward by EYRING in 1935<sup>11)</sup>, which applies exactly to such an elementary reaction as the participating set of particles is practically mechanically independent; it is naturally confronted with a number of ambiguities when extended to the heterogeneous reaction by analogy, where the latter limitation is not fulfilled. The very state of affairs obliged OHH<sup>4)</sup> to generalize the theory<sup>\*)</sup> as mentioned above, as they came upon the heterogeneous reaction of the hydrogen electrode process.

This generalization was elaborated in later works<sup>12)-16)</sup> but the application of the elaborated theory to the hydrogen electrode has not yet been presented in a concrete form. Confusions of the recent followers of GLE mentioned above associated with the negligence of the importance of  $1/f^*$ -factor have stimulated the present author to finish the above presentation with particular stress on the demonstration of the two weak points mentioned above, which might have caused the confusions.

\*) The generalized theory implies the concrete expression for  $f^*$ .

The method of GLE is first followed, covering the first weak point by admitting (V) without verification and giving proper expressions to  $f^*$  and  $a^t$ , although rather intuitively, inevitably in the realm of the GLE theory; the observed dependence of  $i_0$  on  $\eta$  is thus accounted for on the basis of the catalytic mechanism, demonstrating the erroneous conclusion,  $\alpha=2$  <sup>9)17)</sup> instead of  $\alpha=0.5$  to be due to the negligence of  $1/f^*$ -factor. This procedure of following GLE is now shown short of estimating the absolute magnitude of the rate on account of the second weak point, with reference to the failure of BOCKRIS and AZZAM<sup>10)</sup> in calculating the upper bound to the saturation current correctly, who conclude against the catalytic mechanism on the reason of their incorrect result of calculation.

Abandoning now the above procedure, the elaborated general theory of the reaction rate is advanced in its place to found (V) as well as the above mentioned expressions of  $f^*$  and  $a^t$  precisely on its basis; the difficulty of  $\Delta G_0$  is on the other hand overcome in the light of the general theory and the absolute magnitude of the saturation current and its upper limit are calculated with results in conformity with the experiments, thus completing the evidence of the catalytic mechanism against the erroneous disproofs mentioned above.

### § 1. Model of the electrode

Below is described the concrete model adopted previously by OHH<sup>4)</sup> and here too, of the assembly in which the hydrogen electrode process of the catalytic mechanism is going on.

a) The rate-determining step (III) i. e. the recombination of adsorbed hydrogen atoms H(a) proceeds on the net plane of the crystal surface of the electrode material; the seat  $\sigma^*$  of the elementary reaction (III) or the site  $\sigma^*$  of adsorption of its activated complex  $\ast_0$  is the adjacent pair of metal atoms each affording individually a site  $\sigma$  of adsorption for H(a).

b) Only possible states of  $\sigma$  are practically<sup>\*)</sup> those unoccupied and occupied by one hydrogen atom.

c) The  $\sigma^*$ 's or  $\sigma$ 's are respectively of a single kind and physically identical with each other.

d) Each hydrogen atom occupying a  $\sigma$  is situated right above the metal atom appropriate to the  $\sigma$  on the net plane.

\*) It is implied that the probability of occupation of  $\sigma$  by  $\ast_0$  as a part of  $\sigma^*$  is negligible.

e) There exist repulsive interactions between adsorbed hydrogen atoms, as well as between the latter and the activated complex which decay rapidly with increasing distance between hydrogen atoms involved.

## § 2. Formulation of the cathodic current

The cathodic current density  $i_c$  is expressed according to (V) at the condition, where the reversal  $\bar{v}$  of  $\bar{v}$  is negligible, as

$$i_c = k_i a^f / f^* \quad (2.1. a)$$

or specializing  $a^f$  to  $(a^H)^2$  i.e. the activity product of the initial complex of (III) consisting of two adsorbed hydrogen atoms and  $f^*$  to that  $f^{*c}$  of (III), as

$$i_c = k_i (a^H)^2 / f^{*c} \quad (2.1. b)$$

where  $a^H$  is the activity of H(a) and  $k_i$  the appropriate rate constant.

The  $a^H$  is given as

$$a^H = \frac{\theta}{1-\theta} \exp\left(\frac{U}{RT}\right) \quad (2.2)$$

inasmuch as the concentration  $\theta$  of H(a) is effectively raised by  $1/1-\theta$  factor and its chemical potential  $\mu^H = RT \log a^H + \text{const.}$  is increased by an extra reversible work<sup>\*)</sup>  $U$  due to the interaction of the H(a) with surrounding ones. The activity  $a_+^*$  of the activated complex  $\mathcal{X}_c$  is similarly expressed as

$$a_+^* = \frac{c_+^*}{\theta_{\sigma^*(0)}} \exp\left(\frac{U^*}{RT}\right) \quad (2.3)$$

where  $c_+^*$  is the concentration of  $\mathcal{X}_c$ ,  $\theta_{\sigma^*(0)}$  the probability that a particular  $\sigma^*$  is free to access  $\mathcal{X}_c$  i.e. occupied neither by  $\mathcal{X}_c$  nor by H(a) and  $U^*$  the extra reversible work required to bring up  $\mathcal{X}_c$  into a particular unoccupied  $\sigma^*$  due to the interaction of  $\mathcal{X}_c$  with surrounding H(a)'s. The activity coefficient  $f^{*c}$  is in consequence given as

$$\frac{1}{f^{*c}} = \frac{c_+^*}{a_+^*} = \theta_{\sigma^*(0)} \exp\left(-\frac{U^*}{RT}\right) \quad (2.4)$$

The  $i_c$  is now, according to (2.1.b), (2.2) and (2.4),

\*) It is meant by the reversible work the work done in statistical equilibrium in its every step. Cf. §7, ref. (15).

$$i_c = k_i \phi(\theta) \theta^2 \exp\left(\frac{2U - U^*}{RT}\right) \quad (2.5. i)$$

where

$$\phi(\theta) = \theta_{\sigma^*(0)} / (1 - \theta)^2 \quad (2.5. \phi)$$

It follows from (2.5) that the expression  $k_i \theta^2$  for  $i_c$  used by GLE is correct, as they states, only when the coverage is so sparse that  $2U - U^*$  practically vanishes and  $\theta_{\sigma^*(0)}$  as well as  $(1 - \theta)^2$  is practically 1; this condition does not hold, however, in the case of cathodically polarized hydrogen electrode as seen later.

If one writes  $i_c$ , on the other hand, ignoring  $f^{*c}$  as

$$i_c = k_i (a^H)^2 \quad (2.6)$$

instead as (2.1. b),  $i_c$  tends to infinity, as  $\theta$  approaches 1, as seen from (2.2) owing to the factor  $1/1 - \theta$ ; the inclusion of  $f^{*c}$  replaces  $\phi(\theta)$ , which approaches a finite value as  $\theta$  nears 1 as seen later, for the latter factor tending to infinity, on one hand and introduces a factor  $\exp(-U^*/RT)$  of (2.5. i), which plays an important part in the TAFEL'S relation derived from the catalytic mechanism.

OHH assumed<sup>4)</sup>  $U$  and  $U^*$  proportional to  $\theta$  as

$$U = u\theta, \quad U^* = u^*\theta \quad (2.7. a), (2.7. b)$$

where  $u$  or  $u^*$  is the value of  $U$  or  $U^*$  respectively at  $\theta=1$  and expressed<sup>4)</sup>  $\theta_{\sigma^*(0)}$  as

$$\theta_{\sigma^*(0)} = (1 - \theta)^2 \quad (2.8)$$

In the present paper (2.7) will be used as they are, whereas (2.8), which is not necessarily consistent with (2.7), will be revised in the next section in conformity with the latter and e), §1, presupposing that  $U$  or  $U^*$  is the sum of the contributions from the individual surrounding H(a)'s. It will be shown in later sections that this revision of  $\theta_{\sigma^*(0)}$  introduces an unimportant correction, which does not affect the main conclusions of OHH<sup>4)</sup>.

### § 3. $\theta_{\sigma^*(0)}$

Let  $\sigma$  be one of sites in a particular  $\sigma^*$  and  $\sigma'$  be the other. The covered fraction  $\theta$  is identified, on account of c), §1, with the probability that the  $\sigma$  is occupied and  $1 - \theta$  with that unoccupied without any specification to all other sites inclusive of  $\sigma'$  by virtue of b), §1.

The probability  $\theta'$  that  $\sigma'$  is occupied, with the specification that the  $\sigma$  is unoccupied with certainty, should satisfy the relation,

$$a^H = \frac{\theta'}{1-\theta'} \exp\left(\frac{U'}{RT}\right) \quad (3.1)$$

similarly as  $\theta$  does (2.2), where  $U'$  is the extra work due to the interaction under the latter specification i. e. that with H(a)'s outside the  $\sigma^*$ , which is expressed in accordance with (2.7) as

$$U' = u'\theta \quad (3.2)$$

where  $u'$  is  $U'$  at  $\theta=1$  apart from the  $\sigma$ . The  $u'$  is related with  $u$  as

$$u' = u - u_1 \quad (3.3)$$

where  $u_1$  is the part of the extra work due to the interaction between the H(a)'s situated in the same  $\sigma^*$ .

We have now from (2.2), (2.7.a), (3.1), (3.2) and (3.3)

$$\frac{\theta'}{1-\theta'} = \frac{\theta}{1-\theta} \exp\left(\frac{u_1\theta}{RT}\right) \quad (3.4)$$

hence for  $\theta_{\sigma^*(0)}$  i. e. the probability that both  $\sigma$  and  $\sigma'$  are simultaneously unoccupied

$$\theta_{\sigma^*(0)} = (1-\theta)(1-\theta') = \frac{(1-\theta)^2}{1 + \theta \left( \exp\left(\frac{u_1\theta}{RT}\right) - 1 \right)} \quad (3.5. \theta)$$

and for  $\phi(\theta)$  according to (2.5.  $\phi$ )

$$1/\phi(\theta) = 1 + \theta \left( \exp\left(\frac{u_1\theta}{RT}\right) - 1 \right) \quad (3.5. \phi)$$

or in particular

$$\phi(\theta) = 1 \quad \text{at } \theta = 0 \quad (3.6. a)$$

and

$$\phi(\theta) = \exp\left(-\frac{u_1}{RT}\right) \quad \text{at } \theta=1 \quad (3.6. b)$$

Eqs. (2.5.  $\phi$ ) and (3.5.  $\phi$ ) shows that  $\theta_{\sigma^*(0)}$  approximates (2.8) as  $\theta$  nears 0, whereas the other,

$$\theta_{\sigma^*(0)} = (1-\theta)^2 \exp\left(-\frac{u_1}{RT}\right) \quad (3.7)$$

as  $\theta$  does 1, which is valid irrespective of (2.7) in the latter case as shown below.

The probability that a sufficiently distant pair of  $\sigma$ 's are simultaneously unoccupied is  $(1-\theta)^2$  at any value of  $\theta$ , in so far as the interactions between H(a)'s decay sufficiently rapidly with increasing distance according to e), § 1.

Let now two distant  $\sigma$ 's be  $\sigma_a$  and  $\sigma_b$ , and  $\sigma$  which associates  $\sigma_a$  or  $\sigma_b$  in composing respectively particular  $\sigma^*$  i.e.  $\sigma_a^*$  or  $\sigma_b^*$ , be  $\sigma_a'$  or  $\sigma_b'$ . Let  $\sigma_a(0)\sigma_b(0)$  denote the state in which both  $\sigma_a$  and  $\sigma_b$  are unoccupied and  $\sigma_a^*(0)$  that  $\sigma_a^*$  i.e. both  $\sigma_a$  and  $\sigma_a'$  are unoccupied. Both  $\sigma_a'$  and  $\sigma_b'$  are occupied practically with certainty in  $\sigma_a(0)\sigma_b(0)$ , whereas both  $\sigma_b$  and  $\sigma_b'$  of  $\sigma_b^*$  are so in  $\sigma_b^*(0)$  at  $\theta$  near 1. The  $\sigma_a^*(0)$  is now derived from  $\sigma_a(0)\sigma_b(0)$  by transferring the hydrogen atom H<sub>1</sub> occupying  $\sigma_a'$  from there to  $\sigma_b$ ; the appropriate reversible work required is  $u_1$  i.e. that due to the interaction between H<sub>1</sub> and the other hydrogen atom H<sub>2</sub> situated in  $\sigma_b'$ , the reversible work due to the interaction of H<sub>1</sub> with H(a)'s around  $\sigma_a^*$  being compensated by the reversible work due to those around  $\sigma_b^*$ .

Let now the partition function of the whole assembly at the state of  $\sigma_a(0)\sigma_b(0)$  or of  $\sigma_a^*(0)$  be respectively  $Q_1$  or  $Q_2$ . The ratio  $Q_1/Q_2$  equals now the ratio of the probabilities of states  $\sigma_a(0)\sigma_b(0)$  and  $\sigma_b^*(0)$  and related with the reversible work  $u_1$  of deriving  $\sigma_a^*(0)$  from  $\sigma_a(0)\sigma_b(0)$  as

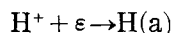
$$RT \log \frac{Q_1}{Q_2} = u_1$$

Eq. (3.7) results readily from the above, remembering the probability  $(1-\theta)^2$  of  $\sigma_a(0)\sigma_b(0)$ .

#### § 4. Dependence of $i_c$ on $\eta$

Eqs. (2.5), (2.7) and (3.5.  $\phi$ ) give  $i_c$  as a function of  $\theta$  and the latter in turn is expressed as a function of  $\eta$  as below.

The step of neutralization of hydrogen ion H<sup>+</sup>, i. e.



must be in partial equilibrium, where  $\epsilon$  is the metal electron in the electrode, in so far as (III) determines the rate. It follows that the chemical potential  $\mu^H$  of H(a) equals the sum of chemical potentials of H<sup>+</sup> and  $\epsilon$  i. e.

$$\mu^H = \mu^{H^+} + \mu^\epsilon \quad (4.1. \mu)$$

The  $\mu^H$ ,  $\mu^{H^+}$  and  $\mu^\epsilon$  are written respectively in the forms,

$$\mu^H = \mu_1^H + RT \log a^H \quad (4.1. H)$$

$$\mu^{H^+} = \mu_1^{H^+} + RT \log a^{H^+} \quad (4.1. H^+)$$

and

$$\mu^\epsilon = \mu_1^\epsilon + RT \log a^\epsilon = \mu_0^\epsilon - F\eta \quad (4.1. \epsilon)$$

where  $a^H$ ,  $a^{H^+}$  and  $a^e$  are activities,  $\mu_1^H$ ,  $\mu_1^{H^+}$ ,  $\mu_1^e$  and  $\mu_0^e$  are respectively constants. We have from (4.1)

$$a^H = a_0^H \exp\left(-\frac{F\eta}{RT}\right) \quad (4.2)$$

where  $a_0^H$  is the value of  $a^H$  at  $\eta=0$ , which is constant at constant  $\mu^{H^+}$  or the constant activity of hydrogen ion in the solution.

It follows from (2.2) and (4.2)

$$RT \log \frac{\theta}{1-\theta} + U + F\eta = \text{const.} \quad (4.3.a)$$

and hence, according to (2.7.a),

$$\frac{\partial \theta}{\partial \eta} = -F / \left\{ \frac{RT}{\theta(1-\theta)} + u \right\} \quad (4.3.b)$$

We have now according to I), (2.5.i), (2.7), (3.5. $\varphi$ ) and (4.3.b)

$$\alpha = \frac{2u - u^* + 2 \frac{RT}{\theta} + RT\gamma}{u + \frac{RT}{\theta(1-\theta)}} \quad (4.4.a)$$

where

$$\gamma = \frac{\partial \log \phi(\theta)}{\partial \theta} = \phi(\theta) \left\{ 1 - \left( 1 + \frac{u_1 \theta}{RT} \right) \exp\left(\frac{u_1 \theta}{RT}\right) \right\} \quad (4.4.r)$$

It follows from (4.4.a) that both  $2 \frac{RT}{\theta}$  in the numerator and  $\frac{RT}{\theta(1-\theta)}$  in the denominator are respectively predominant at sufficiently small  $\theta$ , whereas  $\gamma$  vanishes according to (4.4.r), so that

$$\alpha = 2$$

which has been taken one-sidedly by a number of authors as if it were the whole features of the  $\eta$ -dependence of  $i_0$  derived from the catalytic mechanism. As  $\eta$  decreases,  $\theta$  must approach 1, as (4.3.a) generally requires\*) and in consequence  $\alpha$  vanishes, as  $\frac{RT}{\theta(1-\theta)}$  tends to infinity, while all other terms in (4.4.a) remain finite;  $\alpha$  must hence pass through every value between 2 and 0, as  $\eta$  decreases.

GLE<sup>(6)</sup>) would have arrived at the conclusion,

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\*) The  $\theta$  should increase as  $\eta$  decreases toward its highest possible value 1, since both  $RT \log \frac{\theta}{1-\theta}$  and  $U$  in (4.3.a) increase with  $\theta$ .

$$\alpha = 2 \left/ \left( \frac{1}{1-\theta} + \frac{w\theta}{RT} \right) \right.$$

instead just at  $\alpha=2$ , if they had used the exact expression (2.2) for  $\alpha^H$  in place of (II.a), which leads, according to (4.1), to the  $\theta, \eta$ -relation,

$$RT \log \theta + F\eta = \text{const.}$$

and hence invariably to  $\alpha=2$  according to (II.b). They specify <sup>\*)</sup> the condition under which the above equation holds that the surface is sparsely covered, when the concentration  $n$  <sup>\*\*)</sup> of H(a)'s measures the activity. This condition renders (II.b) to hold as well, as mentioned in § 2. It is however logically imperfect to conclude the catalytic mechanism invalid on the basis of the theoretical inference,  $\alpha=2$ , subject to the latter condition in comparison with the observation  $\alpha=0.5$  resulted possibly under a heavy coverage. KWAN<sup>18)19)</sup> has actually observed that the adsorbed quantity of hydrogen on nickel at 300°C and 0.6 mmHg hydrogen pressure corresponds to 0.6 covered fraction, from which it follows that the covered fraction must be greater than 0.6 on the cathodically polarized hydrogen electrode at room temperature.

PARSONS' argument<sup>17)</sup> on the catalytic mechanism is essentially based on the equation <sup>\*\*\*)</sup>,

$$i_c = k_i (\alpha^{H^+} \alpha^\epsilon)^2 \quad (4.5)$$

where  $k_i$  is constant independent of  $\eta$ ; the conclusion,  $\alpha=2$  follows immediately from (4.5) according to (4.1) invariably over the whole range of  $\theta$  or  $\eta$ .

Eq. (4.5) results from the correct equation (2.1.b) by ignoring  $f^{*c}$  and replacing  $(\alpha^{H^+} \alpha^\epsilon)^2$  for  $(\alpha^H)^2$  in accordance with the partial equilibrium, formulated in (4.1), between the  $I \equiv 2H(a)$  of (III) and the left of the hydrogen electrode reaction,



It follows that (4.5) results, by leaving out  $f^{*c}$ , from every mechanism which has  $\alpha^I$  of the rate-determining step similarly replaceable with  $(\alpha^{H^+} \alpha^\epsilon)^2$  and  $k_i$  constant independent of  $\eta$ ;  $k_i$  is constant as shown in

<sup>\*)</sup> Cf. footnote \*) on p. 582 of ref. (7).

<sup>\*\*)</sup> The  $n$  is the number of atoms of adsorbed hydrogen per square centimeter of electrode surface as defined by GLE and hence is proportional to  $\theta$ .

<sup>\*\*\*)</sup> PARSONS includes  $\alpha^\epsilon$  formally into  $k_i$  and treats  $k_i$  as variable.

§10, if the activated complex of the rate-determining step is indifferent to the electric field as in the case of the catalytic mechanism. Such mechanism would be, besides, for example, that of the rate controlled by the desorption or by the diffusion of hydrogen molecule. The current density of any such mechanism would hence tend to infinity with decreasing  $\eta$ , according to PARSONS<sup>17)</sup>, with  $\alpha$  constantly at 2. The relevance to the catalytic mechanism is restored by including  $f^{*c}$ , which modulates  $(a^H)^c$ , tending itself to infinity with decreasing  $\eta$  according to (4.2), to result in  $i_c$  approaching a finite value instead.

### § 5. Proper fraction of $\alpha$

It may be shown that  $\alpha$  is a proper fraction at the state of cathodically polarized hydrogen electrode, where  $\theta$  exceeds 0.6 according to the foregoing section.

We have from (3.5.  $\phi$ ) and (4.4.  $r$ ),

$$r = \frac{1 - \left(1 + \frac{u_1\theta}{RT}\right) \exp\left(\frac{u_1\theta}{RT}\right)}{1 - \theta + \theta \exp\left(\frac{u_1\theta}{RT}\right)} \quad (5.1. e)$$

which shows that  $r$  is negative because of positive  $u_1$  i. e. of the repulsive interactions. The denominator being positive, we have crossing out 1 in the numerator and the positive term  $1-\theta$  in the denominator in succession,

$$r > - \frac{\left(1 + \frac{u_1\theta}{RT}\right) \exp\left(\frac{u_1\theta}{RT}\right)}{1 - \theta + \theta \exp\left(\frac{u_1\theta}{RT}\right)} > - \left(\frac{1}{\theta} + \frac{u_1}{RT}\right) \quad (5.1. i)$$

The denominator of (4.4.  $\alpha$ ) being positive, we have on the other hand leaving out the negative term  $RT r$  in the numerator,

$$\alpha < \alpha_u \equiv \frac{2u - u^* + \frac{2RT}{\theta}}{u + \frac{RT}{\theta(1-\theta)}} \quad (5.2. u)$$

or replacing the third member of (5.1.  $i$ ) for  $r$ ,

$$\alpha > \alpha_l \equiv \frac{2u - u^* - u_1 + \frac{RT}{\theta}}{u + \frac{RT}{\theta(1-\theta)}} \quad (5.2. l)$$

It is shown now both  $\alpha_u$  and  $\alpha_l$  are positive proper fraction and hence  $\alpha$  itself is too at  $\theta > 0.6$ .

The positive term  $2RT/\theta$  in (5.2.  $u$ ) must be smaller than  $RT/\theta(1-\theta)$  at  $\theta > 0.6$  i. e.

$$0 < \frac{2RT}{\theta} < \frac{RT}{\theta(1-\theta)} \quad (5.3. a)$$

The  $u^*$  may be taken greater than  $u$ , i. e.

$$u^* > u \quad (5.3. b)$$

inasmuch as  $u^*$  or  $u$  is the extra work, according to the definition (2.7), appropriate respectively to the two constituent hydrogen atoms of  $*_c$  or to a single one of H(a). Attributing the interaction to the quantum mechanical exchange repulsion between unbonded hydrogen atoms, OHH<sup>d</sup>) calculated  $u^*$  of  $\sigma^*$  consisting of 3.52 Å distant pair of metal atoms on (110)-plane of nickel crystal, which were found predominantly effective by calculation, at 6.7 Kcal,  $u$  of the same plane at 5.65 Kcal and its component  $u_1$  at 0.31 Kcal. These values of  $u^*$  and  $u$  are in accordance with (5.3. b).

The  $u^*$  does not however include by definition the part of the work due to the interaction between the two constituent hydrogen atoms of  $*_c$  with each other. Let the value of  $u^*$  be  $u_P^*$ , which would be the case, if  $*_c$  happened to assume the configuration of the pair  $P$  of two H(a)'s in  $\sigma^*$  as defined by d), §1. The  $u_P^*$  is given by  $2(u - u_1)$ , as  $2u$  includes twice the part  $u_1$  due to the interaction between the two constituent atoms of  $P$ . The configuration of  $*_c$  must now be taken to lie intermediate between that of  $P$  and that of H<sub>2</sub> molecule. The distance between the two hydrogen atoms of H<sub>2</sub> being smaller than that of  $P$  i. e. between metal atoms of  $\sigma^*$  according to d), §1, the two constituent hydrogen atoms must be drawn more or less together at the state of  $*_c$  or kept remoter from the surrounding H(a)'s compared with those of  $P$ ; the distance of  $*_c$  was worked out by OHH<sup>d</sup>) at 1.25 Å actually intermediate between that 0.75 Å of H<sub>2</sub> and that 3.52 Å of  $P$ . It follows now from e), §1, that  $u^*$  is more or less smaller than  $u_P^*$  or  $2u - 2u_1$  i. e.

$$u^* < 2u - 2u_1 \quad (5.3. c)$$

as satisfied by the above numerical values of  $u^*$ ,  $u$  and  $u_1$ ; as shown by these numerical values, however, the recess of  $u^*$  from  $u_P^*$  is not so much as to break down (5.3. b).

It follows now from (5.3. b) that

$$u^* - 2u > -u$$

or  $2u - u^* < u$

whereas from (5.3. c)

$$u^* - 2u < 0$$

or  $2u - u^* > 0$

and hence

$$0 < 2u - u^* < u \quad (5.3. d)$$

$u_1$  being positive on account of e), §1. Inequalities (5.3. a) and (5.3. d) leads to the conclusion that  $\alpha_p$  of (5.2. u) must be a positive proper fraction.

We have on the other hand similarly as (5.3. a)

$$0 < \frac{RT}{\theta} < \frac{RT}{\theta(1-\theta)} \quad (5.4. a)$$

and from (5.3. b)

$$u^* - 2u + u_1 > -u$$

remembering  $u_1$  is positive, or

$$2u - u^* - u_1 < u$$

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whereas from (5.3.c)

$$0 < 2u - u^* - u_1$$

so that

$$0 < 2u - u^* - u_1 < u \tag{5.4.b}$$

It follows from (5.4) that  $\alpha$ , of (5.2.l) is a positive proper fraction as well and hence  $\alpha$  is too.

The question is now how extensive the positive proper fraction of  $\alpha$  holds. OHH<sup>4)</sup> derived  $\log i_c$  as a function of  $\eta$  by eliminating  $U^*$ ,  $U$  and  $\theta$  from (2.5.i), (4.3.a) and (2.7) identifying  $\phi(\theta)$  with 1 throughout. Using above "theoretical" values of  $u^*$  and  $u$  they have worked out  $\log i_c$ , which runs approximately linearly with  $\eta$  over a range of ca. 0.2 volt with an inclination  $\alpha=0.7$ , tending to a saturation value at  $i_c$  of the order of magnitude of  $10^{-4}$  amp  $\text{cm}^{-2}$  at  $50^\circ\text{C}$ .

We have from (4.4.a) and (5.2.u)

$$\alpha = \alpha_u - \alpha'$$

where

$$\alpha' = -r / \left( \frac{u}{RT} + \frac{1}{\theta(1-\theta)} \right)$$

The above value of  $\alpha$  of OHH<sup>4)</sup> is actually  $\alpha_u$ , inasmuch as  $\phi(\theta)$  is identified with 1 there and hence  $r$  or  $\alpha'$  taken zero according to (4.4.r). The correction term  $\alpha'$  is calculated according to (4.4.r) and (3.5.ϕ) at  $T=323^\circ\text{K}$  for  $u=5.65$  Kcal and  $u_1=0.31$  Kcal, as

$\theta$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\alpha'$	0	0.0050	0.014	0.023	0.032	0.040	0.046	0.050	0.050	0.041	0

The approximate value  $\alpha_u$  of  $\alpha$  or better its value corrected for  $\alpha'$  roughly reproduces the observed value around 0.55, which latter is however kept nearly constant, as observed, over a range of  $\eta$  as much as 0.5 volt. The above theoretical saturation value is moreover smaller than the observed current density and in consequence must be even appreciably smaller than the actual saturation value, if any. This discrepancy was taken by LUKOWZEW, LEWINA and FRUMKIN<sup>22)</sup> as disproving the catalytic mechanism but theoretical value of  $u^*$  or  $u$  included in the expression of the saturation current is too crude for the relevant theoretical saturation current to be reliable even in the order of magnitude<sup>23)</sup>.

These values might now alternatively be estimated on the empirical basis as below. KWAN<sup>18) 19)</sup> has found that the heat of adsorption of hydrogen on nickel decreases by ca. 15 Kcal/mol  $\text{H}_2$  as  $\theta$  increases from

0 to 0.3. This decrease must be attributed as shown in §13\*) to the increase of  $2U$  or of  $2u\theta$  according to (2.7.a), so that

$$u = \frac{15}{2 \times 0.3} = 25 \text{ Kcal} \quad (5.5)$$

Using this revised value it is shown as below that  $\alpha$  varies actually sufficiently slowly over a range *ca.* 0.4 volt of  $\eta$  and that the above theoretical saturation value  $10^{-4}$  amp  $\text{cm}^{-2}$  should be multiplied by a factor  $2 \times 10^6$ , which account for the above experimental facts in confirmation of the catalytic mechanism.

We have from (4.4. a)

$$\alpha = 2 - \frac{u^*}{u} + \alpha_r \quad (5.6. a)$$

where

$$\alpha_r = \frac{RT}{u\theta} \left( 2 + r\theta - \frac{\alpha}{1-\theta} \right) \quad (5.6. r)$$

The  $u_1$  in (5.1.e) of  $r$  is estimated from the above revised value of  $u$  by multiplying the latter by the ratio of the "theoretical values" of  $u_1$  and  $u$  as

$$u_1 = 25 \times \frac{0.31}{5.65} \text{ Kcal} = 1.4 \text{ Kcal} \quad (5.7)$$

The  $r$ ,  $\phi(\theta)$  and  $\alpha_r$  are calculated at 25°C from (5.5) and (5.7) according to (5.1.e), (3.5.  $\phi$ ) and (5.6. r) as shown in the Table, taking  $\alpha$  at the observed value, 0.52<sup>20)</sup> at 25°C.

$\theta$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\phi(\theta)$	0.98	0.90	0.77	0.62	0.48	0.36	0.26	0.19	0.14
$r(\theta)$	0.53	1.18	1.83	2.38	2.79	3.04	3.17	3.22	3.23
$\alpha_r$	0.32	0.13	0.06	0.01	-0.02	-0.04	-0.07	-0.09	-0.16
$2u - u^*$ Kcal	5.0	9.8	11.5	12.8	13.5	14.0	14.8	15.3	17.0

The Table shows that  $\alpha_r$  decreases with increasing  $\theta$  slowly from -0.04 at  $\theta=0.6$  to -0.16 at  $\theta=0.9$  leaving  $\alpha$  approximately constant throughout, while  $\eta$  decreases by *ca.* 0.4 volt according to (4.3. a), (2.7. a) and (5.5).

The saturation current density  $i_s$  or  $i_c$  at  $\theta=1$  is given, on the other hand, according to (2.5. i) and (2.7) as

$$i_s = k_e \phi(1) \exp \left( \frac{2u - u^*}{RT} \right)$$

where  $\phi(1)$  is  $\phi(\theta)$  at  $\theta=1$ , given by (3.6. b). It follows that  $i_s$  of OHH<sup>4)</sup> must be multiplied by a factor,

\*) Cf. (13.6) derived on the basis of the generalized theory of reaction rate.

$$\frac{\phi(1)}{\phi(1)'} = \frac{\exp\left(\frac{2u-u^*}{RT}\right)}{\exp\left(\frac{2u-u^*}{RT}\right)'}$$

where the function with or without prime denotes that used by OHH or the revised one.

The lowest row of the above Table gives  $2u-u^*$  computed from the observed value 0.52<sup>20)</sup> of  $\alpha$ , (5.5), (5.6) and the value of  $\tau$  given in the Table; averaging these values over  $\theta$  values, 0.6 and above, given in the Table, we have

$$2u-u^* = 15.3 \text{ Kcal} \quad (5.8)$$

which contrasts with the theoretical value,

$$2u-u^* = 4.6 \text{ Kcal} \quad (5.9)$$

Remembering  $\phi(1)'=1$  we have from (3.6.b), (5.7), (5.8) and (5.9)

$$\frac{\phi(1)}{\phi(1)'} = \frac{\exp\left(\frac{2u-u^*}{RT}\right)}{\exp\left(\frac{2u-u^*}{RT}\right)'} = \exp\left(\frac{15.3-1.4-4.6}{RT}\right)$$

which contributes a factor  $2 \times 10^6$  at 50°C, by which the theoretical value  $10^{-4}$  amp  $\text{cm}^{-2}$  of OHH<sup>4)</sup> is to be multiplied, to give  $i_s = 2 \times 10^2$  amp  $\text{cm}^{-2}$  at 50°C.

So far we have used (2.5.i) for calculating the relative variation of  $i_c$  but not its absolute value. After a semi-quantitative explanation is given to  $\alpha$  in the next section for being a proper fraction near 0.5, the absolute rate will be dealt with in later sections.

### § 6. $\alpha \doteq 0.5$

Let us first assume that  $\sigma$ 's are arrayed in a plane square pattern, each pair of adjacent two ones providing a  $\sigma^*$ , that the deviation of the configuration of  $\kappa_c$  from that of  $P^*$ ) i.e. a pair of H(a)'s in  $\sigma^*$  is negligible and that the repulsive interactions exist only between directly neighbouring hydrogen atoms inclusive of those of  $\kappa_c$ . As  $\kappa_c$  has six direct neighbours, while H(a) four ones, we have

$$u^*/u = \frac{6}{4} = 1.5 \quad (6.1)$$

As  $\alpha$  is given, neglecting  $\alpha_r$  in (5.6) according to the foregoing section, as

$$\alpha = 2 - u^*/u \quad (6.2)$$

we have

$$\alpha = 0.5$$

It follows now from (I), (2.1.b) and (4.2) that

---

<sup>\*)</sup> Cf. p. 67, par. 2

$$\alpha = 2 - \frac{RT}{F} \frac{\partial \log f^{*c}}{\partial \eta} \quad (6.3)$$

and from the comparison of (6.2) and (6.3) that  $1/f^{*c}$ -factor of the rate expression (2.1) provides  $u^*/u$ , which amends the classical value 2 of  $\alpha$  to the observed one ca. 0.5, or that its negligence is responsible for the erroneous conclusion that  $\alpha=2$  throughout.

The  $\alpha$  is more or less distorted from 0.5, besides by the neglect of  $\alpha_r$  in (5.6.a), along with the deviation from the above idealized model; it increases according to (6.2), as the two hydrogen atoms of  $P$  are drawn together to form  $\times_c$ , reducing  $u^*$  as mentioned in the foregoing section, whereas it decreases with the deviation of  $\sigma^*$  from the above idealized one to that of 3.52 Å distant pair of  $\sigma$ 's on (110)-plane as shown below. Two circles in Fig. 1, (a) show  $\sigma^*$  and dots six directly neighbouring  $\sigma$ 's, four among them being 2.49 Å and two others 3.52 Å respectively distant from the nearest  $\sigma$  of  $\sigma^*$ .

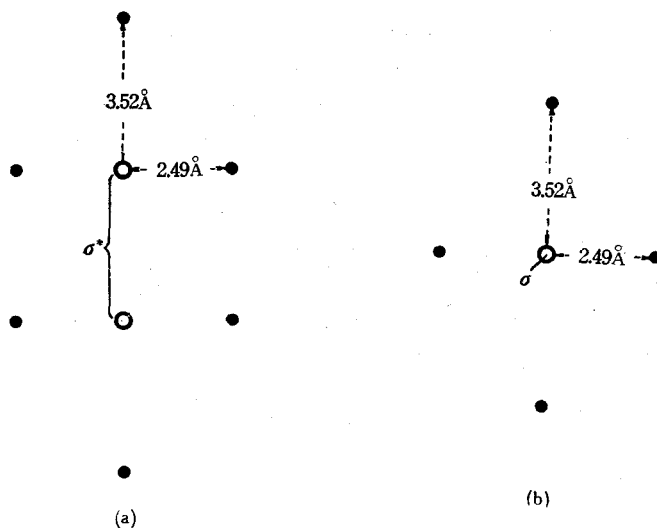


Fig. 1.

Arrangement of sites on (110)-plane of nickel

The circle of Fig. 1, (b) shows  $\sigma$  and four dots direct neighbouring ones, the two being 2.49 Å and the other two 3.52 Å respectively distant from the  $\sigma$  of the circle. Two components respectively of  $u^*$  or  $u$  due to the remoter neighbours must be smaller than the remaining ones according to e), §1,  $u^*/u$  exceeds 1.5 or  $\alpha$  recedes 0.5 according to

(6.2) by this cause, reducing  $\alpha$  to nil in the extreme case of negligible contribution from the remoter neighbours.

### § 7. Saturation current at extreme cathodic polarization

BOCKRIS and AZZAM<sup>10)</sup> have observed a tendency of the cathodic current to approach a saturation value, beginning at the current density of the order  $10^1$  amp cm<sup>-2</sup> and at the cathodic polarization of 0.6 volt. These authors concluded that their result disproved the catalytic mechanism on the reason that they calculated the upper bound to the saturation current on its basis at  $\sim 1$  amp cm<sup>-2</sup> less than the observed current density. BOCKRIS and AZZAM<sup>10)</sup> express the current density  $i_c$  as

$$i_c = 2 \cdot 10^{-18} F \frac{kT}{h} \theta^2 \exp\left(-\frac{\Delta G_0}{RT}\right) \quad (7.1)$$

where the factor  $10^{-18}$  is the square of the surface concentration in mol cm<sup>-2</sup> of hydrogen atoms fully covering  $10^{15}$  sites cm<sup>-2</sup> of the electrode surface. Putting  $\theta=1$  and  $\Delta G_0=0$  in the above equation, BOCKRIS and AZZAM<sup>10)</sup> calculate  $i_u$  i. e.

$$i_u = 2 \cdot 10^{-18} F \frac{kT}{h} \quad (7.2)$$

as above.

We might investigate their proceeding by varying the magnitude of the unit of surface area. Changing it from cm<sup>2</sup> to m<sup>2</sup>, the numerical factor on the right of (7.1) is  $2 \times 10^{-10}$  instead of  $2 \times 10^{-18}$  and the right should give with this factor  $i_u$  in amp m<sup>-2</sup> instead in amp cm<sup>-2</sup>. The "upper bound" of (7.2) is now  $10^3$  amp m<sup>-2</sup> or  $10^1$  amp cm<sup>-2</sup> in place of 1 amp cm<sup>-2</sup>. We see that any value we like of  $i_u$  is obtained by selecting the magnitude of the unit. This is, however, because of the dimensional inconsistency of (7.2), which shows the argument of BOCKRIS and AZZAM<sup>10)</sup> is invalid.

The correct expression for  $i_c$  is given in accordance with (2.1), by multiplying the right of (7.1) by  $(f^H)^2$  to make up  $(a^H)^2$  from the square,  $10^{-18} \theta^2$  of the surface concentration and dividing the result by  $f^{*c}$  as

$$i_c = 2 \cdot 10^{-18} F \frac{kT}{h} \theta^2 \frac{(f^H)^2}{f^{*c}} \exp\left(-\frac{\Delta G_0}{RT}\right) \quad (7.3)$$

provided that the standard states of the adsorbed atoms and the activated complex implied in  $\Delta G_0$  are respectively those of unit activity.

Writing  $f^H$  according to (2.2) as<sup>\*</sup>

$$f^H = \frac{\exp\left(\frac{U}{RT}\right)}{1 - \theta} \quad (7.4)$$

(7.3) is given by (2.4), (2.5.φ) and (7.4)<sup>\*</sup> as

$$i_o = 2 \cdot 10^{-18} F \frac{kT}{h} \theta^2 \phi(\theta) \exp\left(\frac{2U - U^*}{RT}\right) \exp\left(-\frac{\Delta G_o}{RT}\right) \quad (7.5)$$

If the unit area is  $n$ -folded, the numerical value of the left increases by a factor  $n$ , whereas the coefficient of the exponential function  $n^2$ -folded. The exponential function is now in accordance with GLE's theory the ratio of the activity of the activated complex to the square of the activity of the adsorbed hydrogen atom at equilibrium between them. The  $n$ -fold magnification of the unit area multiplies the magnitude of the activity of the standard state of the activated complex as well as that of the adsorbed hydrogen atom by the same factor  $n$ . The exponential factor is hence multiplied by a factor  $1/n$ , so that (7.3) remains valid independent of the selection of the unit of area, as it should of course do.

The numerical value of the exponential function and hence of  $\Delta G_o$  depends thus on the selection of the unit of the surface area;  $\Delta G_o$  may well be negative or the exponential function greater than unity at a particular selection of unit. It is the fallacy of BOCKRIS and AZZAM<sup>10)</sup> that they have taken the exponential factor necessarily smaller than unity. Their claim against the catalytic mechanism is hence of no ground. The upper bound aimed at by BOCKRIS and AZZAM<sup>10)</sup> i.e. the greatest possible current maintained by the catalytic mechanism is correctly  $2 \times 10^9$  amp  $\text{cm}^{-2}$ , as worked out in §12 on the basis of the general theory, which conforms with the catalytic mechanism underlying their experiment<sup>10)</sup>.

So far we have extended GLE method by introducing the expressions of activity coefficients additionally for demonstrating current and important delusions in the application of the method to the heterogeneous reaction. It seems now beyond the capacity of this procedure however to predict the absolute magnitude of the saturation current

<sup>\*</sup>) The activity given by (2.2), from which (7.4) is derived is referred to the concentration  $\theta$  instead to  $\text{mol cm}^{-2}$ , but the activity coefficient, which is dimensionless, is invariant independent of the sort of unit of the surface concentration.

on the basis of (7.5) on account of the vague conception of  $\Delta G_0$  extended to the heterogeneous reaction by analogy. Neither very cogent is the above introduction of the activity coefficients in the realm of this procedure

We will now give it up and put forward the general theory for establishing the functions introduced above on one hand and for estimating the magnitude of the saturation current density at higher  $-\eta$  for completing the verification of the catalytic mechanism on nickel on the other hand.

### § 8. General theory

The rate  $\bar{v}$  of any thermal elementary reaction is expressed as

$$\bar{v} = \frac{kT}{h} p^*/p^{I^*} \quad (8.1. \bar{v})$$

and the rate  $\bar{v}$  of its reversal as

$$\bar{v} = \frac{kT}{h} p^*/p^{F^*} \quad (8.1. \bar{v})$$

where  $p^*$  is the BOLTZMANN factor of the chemical potential of a single activated complex  $\ast$  existing in the assembly in question<sup>\*)</sup> and  $p^I$  or  $p^F$  the BOLTZMANN factor of the chemical potential respectively of the initial complex  $I$  or of the final complex  $F$  of the elementary reaction; the transmission coefficient is omitted for the sake of simplicity.

Eq. (8.1) is developed in different forms for various particular cases of homogeneous or heterogeneous reactions, with the aid of theorems<sup>15)</sup> quoted below so far as necessary for the present application.

Let  $\delta$  be any set of particles inclusive of  $\ast$ ,  $I$  and  $F$ , and  $p^\delta$  be the BOLTZMANN factor of the chemical potential of  $\delta$ .

i) If  $\delta$  consists of statistically independent parts,  $\delta_1, \dots, \delta_i, \dots, \delta_s$ , as  $I$  of (III), which consists of two statistically independent H(a)'s,

$$p^\delta = \prod_{i=1}^{i=s} p^{\delta_i} \quad (8.2)$$

ii) If two states  $A$  and  $B$  of  $\delta$  are in equilibrium, inclusive of partial equilibrium, with each other,

\*) Cf. ref. (15), page 45.

\*\*) It is by no means maintained that there exists physically a single activated complex in the assembly in question but stated simply that using the appropriate  $p^*$ , the rate is given "mathematically" by (8.1); cf. refs. (12) and (13).

$$p^A = p^B \quad (8.3)$$

iii) Let  $\Sigma$  be any cell to house  $\delta_i$  such as a cell in a homogeneous phase or a site  $\sigma$  or  $\sigma^*$  of adsorption at the boundary surface; then

$$p^{\delta_i} = \frac{\theta_{\Sigma(0)}}{\theta_{\Sigma(\delta_i)}} q^{\delta_i} \quad (8.4)$$

where  $\theta_{\Sigma(0)}$  is the probability that  $\Sigma$  is occupied by none,  $\theta_{\Sigma(\delta_i)}$  that  $\Sigma$  is occupied by one  $\delta_i$  and  $q^{\delta_i}$  the BOLTZMANN factor of the reversible work required to bring up  $\delta_i$  from its standard state up to a specified, preliminarily evacuated  $\Sigma$ .

iv) It is derived from (8.4) that

$$p^{\delta_i} = Q^{\delta_i} / N^{\delta_i} \quad (8.5.p)$$

where

$$Q^{\delta_i} = \lim_{|\Sigma| \rightarrow 0} \frac{q^{\delta_i}}{|\Sigma|} \quad (8.5.Q)$$

$$N^{\delta_i} = \lim_{|\Sigma| \rightarrow 0} \frac{\theta_{\Sigma(\delta_i)}}{|\Sigma|} \quad (8.5.N)$$

and  $|\Sigma|$  is the volume of  $\Sigma$ . In the case of dilute gas phase,  $Q^{\delta_i}$  is the partition function of a single gas molecule  $\delta_i$  in unit volume and  $N^{\delta_i}$  its concentration.

### §9. Activity and activity coefficient

Below will be deduced expressions of activity  $a^{\delta_i}$ , activity coefficient  $f^{\delta_i}$  and standard chemical potential  $\mu_1^{\delta_i}$  with special reference to  $\delta_i$  in  $\Sigma$  on the boundary surface from the general theory introduced in the foregoing section.

The chemical potential  $\mu^{\delta_i}$  of  $\delta_i$  is given according to the definition of  $p^{\delta_i}$  and (8.4), as

$$\mu^{\delta_i} = -RT \log p^{\delta_i} = RT \log \frac{\theta_{\Sigma(\delta_i)}}{\theta_{\Sigma(0)} q^{\delta_i}} \quad (9.1)$$

or expressed as

$$\mu^{\delta_i} = \mu_1^{\delta_i} + RT \log a^{\delta_i} \quad (9.2.\mu)$$

$$a^{\delta_i} = f^{\delta_i} N^{\delta_i} \quad (9.2.a)$$

according to the definitions of  $a^{\delta_i}$ ,  $f^{\delta_i}$  and  $\mu_1^{\delta_i}$ , where  $N^{\delta_i}$  is the surface concentration of  $\delta_i$  housed in  $\Sigma$ , which is proportional to  $\theta_{\Sigma(\delta_i)}$ , i. e.

$$N^{\delta_i} = K^{\delta_i} \theta_{\Sigma(\delta_i)} \quad (9.3)$$

the proportionality constant  $K^{\delta_i}$  depending on the definition of  $N^{\delta_i}$ .  
Writing (9.1) as

$$\mu^{\delta_i} = -RT \log r K^{\delta_i} + RT \log \frac{r}{q^{\delta_i} \theta_{\Sigma(0)}} N^{\delta_i}$$

and comparing the latter with (9.2), we have

$$\mu_1^{\delta_i} = -RT \log r K^{\delta_i}, \quad f^{\delta_i} = \frac{r}{q^{\delta_i} \theta_{\Sigma(0)}} \quad (9.4. \mu), (9.4. f)$$

where  $r$  is a constant determined by the condition that the appropriate activity coefficient  $f^{\delta_i}$  approaches 1, as certain constituents  $\delta_j$ 's of variable concentrations  $N^{\delta_j}$ 's of the assembly, possibly inclusive of  $\delta_i$  itself, respectively tend to vanish. Let the value  $q^{\delta_i}$  or  $\theta_{\Sigma(0)}$  at the latter extreme case be  $q_0^{\delta_i}$  or  $\theta_{\Sigma(0),0}$ ; then

$$r = q_0^{\delta_i} \theta_{\Sigma(0),0}, \quad f^{\delta_i} = \frac{q^{\delta_i}}{q_0^{\delta_i}} \frac{\theta_{\Sigma(0),0}}{\theta_{\Sigma(0)}} \quad (9.5. r), (9.5. f)$$

and

$$\mu_1^{\delta_i} = -RT \log q_0^{\delta_i} \theta_{\Sigma(0),0} K^{\delta_i} \quad (9.5. \mu)$$

In the special case of §1, when  $\Sigma$  is  $\sigma$  or  $\sigma^*$ ,  $\delta_i$  is H or  $\times_c$  and  $\delta_j$  is H(a) alone, we have, according to b) there

$$\theta_{\sigma(0),0} = 1, \quad \theta_{\sigma \times_c(0),0} = 1 \quad (9.6. a), (9.6. b)$$

The  $\theta_{\sigma(H)}$  is identified with the covered fraction  $\theta$  and  $\theta_{\sigma(0)}$  with  $1-\theta$  according to b) and c), §1, i. e. as

$$\theta_{\sigma(H)} = \theta, \quad \theta_{\sigma(0)} = 1-\theta \quad (9.7. a), (9.7. b)$$

whereas the probability  $\theta_{\sigma \times_c(\sigma^*)}$  that a single  $\times_c$  in the assembly resides in a particular  $\sigma^*$ , equals the reciprocal of the total number  $G$  of  $\sigma^*$  there i. e.

$$\theta_{\sigma \times_c(\sigma^*)} = 1/G \quad (9.8)$$

The reversible work  $-RT \log q^H$  or  $-RT \log q^{*c}$  is expressed on the other hand as the sum of that  $-RT \log q_0^H$  or  $-RT \log q_0^{*c}$ , in the absence of H(a)'s and the extra work  $U$  or  $U^*$  due to their presence, as

$$-RT \log q^H = -RT \log q_0^H + U \quad (9.9. H)$$

$$-RT \log q^{*c} = -RT \log q_0^{*c} + U^* \quad (9.9. *)$$

Particular expressions of  $a^{\delta\epsilon}$ ,  $f^{\delta\epsilon}$ ,  $\mu_1^{\delta\epsilon}$  and  $N^{\delta\epsilon}$  are now according to equations from (9.2) to (9.9)

$$a^H = f^H K^H \theta, \quad f^H = \frac{\exp\left(\frac{U}{RT}\right)}{(1-\theta)}, \quad \mu_1^H = -RT \log q_0^H K^H, \quad N^H = K^H \theta$$

(9.10.a), (9.10.f), (9.10.μ), (9.10.N)

$$a^* = f^{*c} K^{*c} / G, \quad f^{*c} = \frac{\exp\left(\frac{U^*}{RT}\right)}{\theta_{\sigma^{*(0)}}}, \quad \mu_1^{*c} = RT \log q_0^{*c} K^{*c}, \quad N^{*c} = K^{*c} / G$$

(9.11.a), (9.11.f), (9.11.μ), (9.11.N)

Eqs. (9.10) and (9.11) establish (2.2), (2.3), (2.4) and (7.4) introduced rather intuitively previously, with proper identification i.e. of  $K^H$  with 1 and of  $a_+^*$  or  $c_+^*$  there with  $a^{*c}$  or  $N^{*c}$  here.

Eq. (9.1) is alternatively written according to (8.5) as

$$\mu^{\delta\epsilon} = RT \log \frac{N^{\delta\epsilon}}{Q^{\delta\epsilon}}$$

from which we have similarly

$$\mu_1^{\delta\epsilon} = RT \log Q_0^{\delta\epsilon}$$

and

$$f^{\delta\epsilon} = \frac{Q_0^{\delta\epsilon'}}{Q^{\delta\epsilon}}$$

as deduced previously<sup>\*)</sup>, where  $Q_0^{\delta\epsilon}$  is  $Q^{\delta\epsilon}$  at the vanishing concentrations of variable components.

Below will be derived (3.4) in addition, which is basic to (3.5.θ) of  $\theta_{\sigma^{*(0)}}$ . At given chemical potential of H(a) we have, according to the definition of  $p^{\delta\epsilon}$ <sup>\*\*)</sup>, for  $\theta$  as well as for  $\theta'$  according to (8.4) and (9.7)

$$p^H = \frac{1-\theta}{\theta} q^H$$

$$p^H = \frac{1-\theta'}{\theta'} q^{H'}$$

where  $q^{H'}$  is appropriate to a site  $\sigma'$  whose partner site  $\sigma$  in a particular  $\sigma^*$  is unoccupied with certainty. Expressing  $q^H$  and  $q^{H'}$  in accordance

<sup>\*)</sup> Cf. ref. 15, § 28.

<sup>\*\*)</sup> Cf. § 8.

with (9.9.H) and (2.7. a) as

$$q^H = q_0^H \exp\left(-\frac{u\theta}{RT}\right), \quad q^{H'} = q_0^{H'} \exp\left(-\frac{u'\theta}{RT}\right)$$

we have (3.4) from the above four equations remembering (3.3).

### §10. Negligence of $f^{**}$

It is shown in this section on the basis of the general theory that (4.5) with constant  $k_i$  results as stated in §4 by ignoring the activity coefficient  $f^*$  of the activated complex, for any mechanism of the rate-determining step whose initial complex is in partial equilibrium with the left of (4.6) and activated complex has energy not affected by electric field. The rate  $\bar{v}$  of the rate-determining step is given according to (8.1.  $\bar{v}$ ) and (8.4) as

$$\bar{v} = \frac{kT}{h} \frac{\theta_{\Sigma^{*(0)}}}{\theta_{\Sigma^{*(*)}}} \frac{q^*}{p^f}$$

or as

$$\bar{v} = \frac{kT}{h} G_{\Sigma^{*}} \theta_{\Sigma^{*(0)}} \frac{q^*}{p^f}$$

expressing  $\theta_{\Sigma^{*(*)}}$  by the reciprocal of the total number  $G_{\Sigma^{*}}$  of  $\Sigma^{*}$  i. e.  $\Sigma$  for  $*$  in the assembly\*) as

$$\theta_{\Sigma^{*(*)}} = 1/G_{\Sigma^{*}}$$

The cathodic current density  $i_c$  is obtained at the condition where the reverse rate is negligible, by dividing  $\bar{v}$  by the area  $A$  of the electrode surface and the stoichiometric number  $\nu(r)^{**})$  and by multiplying the result by the electricity  $2F/N_A$  associated with once the overall reaction, as

$$i_c = \frac{2FkT}{N_A \nu(r) h} \frac{G_{\Sigma^{*}}}{A} \theta_{\Sigma^{*(0)}} \frac{q^*}{p^f} \quad (10.1)$$

where  $N_A$  is the AVOGADRO'S number.

Eq. (10.1) may be written according to (9.5.  $f$ ) in the form, i. e.

$$i_c = \frac{k'}{f^{*} p^f} \quad (10.2. i)$$

\*) Cf. ref. (15), §24.

\*\*\*) Cf. §26 and 27 of ref. (15) and HORIUTI and SUGAWARA (this volume, p. 1).

where

$$k' = \frac{2FkTG_{\Sigma^*}}{N_A\nu(r)hA} \theta_{\Sigma^*(0),0} q_0^* \quad (10.2.k)$$

$$f^* = \frac{q_0^* \theta_{\Sigma^*(0),0}}{q^* \theta_{\Sigma^*(0)}} \quad (10.2.f)$$

The condition of the partial equilibrium of  $I$  with the left of (4.6) is given on the other hand according to (8.2) and (8.3) as

$$p^I = (p^{H^+} p^e)^2 \quad (10.2.p)$$

Eq. (10.2.i) and (10.2.p) give, with reference to (4.1) and the definition,  $p^{\delta} = \exp\left(-\frac{\mu^{\delta}}{RT}\right)$ ,

$$i_c = \frac{k_i}{f^*} (a^{H^+} a^e)^2 \quad (10.3)$$

where  $k_i$  differs from  $k'$  by an unimportant constant factor. Eq.(10.3) reproduces (4.5) by leaving out  $f^*$ , where  $k_i$  is, according to (10.2.k), constant independent of the electrode potential provided that the reversible work  $-kT \log q_0^*$  appropriate to  $\ast$  is not affected by the associated variation of the electric field at the electrode surface. The previous statement with regard to (4.5) has now been established.

### § 11. Cathodic current of the catalytic mechanism

We will now specialize ourselves to the catalytic mechanism and formulate the cathodic current density  $i_c$  on the basis of the general theory for examining (7.5) introduced in extension of the GLE method.

The  $p^I$  of (8.1.  $\bar{v}$ ) is expressed for  $I \equiv 2H(a)$  according to (8.2), (8.4), (9.7) and (9.9.H) as

$$p^I \equiv (p^{H^+})^2 = \left\{ q_0^H \frac{1-\theta}{\theta} \exp\left(-\frac{U}{RT}\right) \right\}^2 \quad (11.1.I)$$

and  $p^*$  for  $\ast_c$  according to (8.4), (9.8) and (9.9.  $\ast$ ) as

$$p^* \equiv p^{\ast_c} = G\theta_{\sigma^*(0)} q_0^{\ast_c} \exp\left(-\frac{U^*}{RT}\right) \quad (11.1.\ast)$$

Dividing through the equation for  $\bar{v}$  obtained from (8.1.  $\bar{v}$ ) and (11.1) by  $A$ , we have, referring to (2.5.  $\phi$ ),

$$\bar{v}_1 = \frac{kT}{h} G_1 \phi(\theta) \theta^2 \exp\left(\frac{2U-U^*}{RT}\right) \cdot \frac{q_0^{\ast_c}}{(q_0^H)^2} \quad (11.2)$$

where  $\bar{v}_1 = \bar{v}/A$  and  $G_1 = G/A$ .

The  $i_c$  is obtained, similarly as in the case of (10.1), by multiplying the above equation by charge  $2F/N_A$  associated with one act of the overall reaction, remembering  $\nu(r)=1$  in this case, as

$$i_c = \frac{2F}{N_A} \frac{kT}{h} G_1 \theta^2 \phi(\theta) \exp\left(\frac{2U-U^*}{RT}\right) \cdot \frac{q_o^{*c}}{(q_o^H)^2} \quad (11.3)$$

Eq.(11.3) is of course obtained from (10.1) by specializing  $\nu(r)$  to 1,  $G_{\Sigma^*}/A$  to  $G_1$ ,  $\Sigma^*$  to  $\sigma^*$  and  $p^f$  to that of (11.1.I) for the catalytic mechanism.

The  $\mu_1^H$  or  $\mu_1^{*c}$  is given on the other hand by (9.10. $\mu$ ) or (9.11. $\mu$ ) choosing unit concentration at mol cm<sup>-2</sup> as did by BOCKRIS and AZZAM i. e.  $K^H$  or  $K^*$  at  $10^{-9}$  or  $G_1/N_A$  respectively, as

$$\mu_1^H = -RT \log q_o^H \times 10^{-9} \quad (11.4.H)$$

$$\mu_1^{*c} = -RT \log \frac{G_1 q_o^{*c}}{N_A} \quad (11.4.*)$$

Writing now (11.3) in the form,

$$i_c = 2 \cdot 10^{-18} F \frac{kT}{h} \cdot \theta^2 F(\theta) \exp\left(\frac{2U-U^*}{RT}\right) \cdot \frac{G_1}{N_A} \frac{q_o^{*c}}{(q_o^H \times 10^{-9})^2} \quad (11.5)$$

we see that the last factor of (11.5) is, according to (11.4),

$$\frac{G_1 q_o^{*c}}{N_A (q_o^H \times 10^{-9})^2} = \exp\left(-\frac{\mu_1^{*c} - 2\mu_1^H}{RT}\right) \quad (11.6)$$

The  $\mu_1^{*c} - 2\mu_1^H$  in (11.6) is the free energy difference between standard states of  $\ast_c$  and  $2H(a)$  respectively of unit activity i. e. just  $\Delta G_o$  of (7.5);  $G_1$  on the left of (11.6) being the number of  $\sigma^*$  per unit area, whereas  $10^{-9}$  the number of mols per cm<sup>2</sup> of hydrogen atoms fully covering the surface, we see clearly that the exponential factor varies with the magnitude of the unit of area as stated in §7, and by diminishing its magnitude, it may even become greater than unity as mentioned there. Eq. (7.5) has now been established along with  $\Delta G_o$  of the heterogeneous reaction being statistical mechanically clearly defined.

We will now proceed to estimate the absolute magnitude of the saturation current and its upper bound on the basis of (11.3).

§ 12. Upper bound to the saturation current

Eq. (11.3) gives the saturation current by substituting 1 for  $\theta^2$ ,  $u$  or  $u^*$  respectively for  $U$  or  $U^*$ , and the limiting value  $\exp\left(-\frac{u_1}{RT}\right)$  of (3.6.b) for  $\phi(\theta)$ , as

$$i_c = \frac{2F}{N_A} \frac{kT}{h} G_1 \cdot \frac{q_0^{*\sigma}}{(q_0^H)^2} \cdot \exp\left(\frac{2u - u_1 - u^*}{RT}\right) \quad (12.1)$$

The product of the second and the third factor of (12.1) is the BOLTZMANN factor of  $w$ , i. e.

$$w = -RT \log q_0^{*\sigma} + u^* - \left\{ -2RT \log q_0^H + u_1 + 2(u - u_1) \right\}$$

The sum of the first and the second terms on the right of the above equation is, according to §8, (9.9.\* ) and (2.7.b), the reversible work  $-RT \log q_0^{*\sigma}$  at  $\theta=1$ ; the sum of the first and the second terms in the parenthesis  $\{ \}$  is similarly according to (9.9.H) and (2.7.a) the reversible work required to form a pair of H(a)'s in an unoccupied  $\sigma^*$  with the surrounding  $\sigma$ 's completely unoccupied, inasmuch as the interaction exists then only between H(a)'s of the pair. The latter reversible work increases by the last term  $2(u - u_1)$ , as the surrounding  $\sigma$ 's are fully occupied, each H(a) of the pair contributing the extra work  $u - u_1$ ; the content of the parenthesis is in consequence the reversible work required to build up a pair of H(a)'s in a particular unoccupied  $\sigma^*$  with surrounding  $\sigma$ 's fully occupied. The  $w$  is hence the reversible work for converting a pair of H(a)'s situated in a  $\sigma^*$  into the  $\times_c$  there with surrounding  $\sigma$ 's fully occupied;  $\frac{kT}{h} \exp\left(-\frac{w}{kT}\right)$  being now according (12.1) the specific rate of transition of a particular pair of H(a)'s in a  $\sigma^*$  into  $H_2$ ,  $w$  must be positive, in so far as the pair should exist with such a stability as (III) determines the rate.

The BOLTZMANN factor of  $w$  or the product of the second and the third factor of (12.1) must hence be less than 1 and in consequence the first factor gives the correct upper bound  $i_u$  to the saturation current i. e.

$$i_u = \frac{2F}{N_A} \frac{kT}{h} G_1 \quad (12.2. a)$$

which is now dimensionally consistent in distinction from (7.2) of

BOCKRIS and AZZAM<sup>10)</sup>. The  $G_1$  is of order of magnitude of  $10^{15}$  and is particularly  $1 \times 10^{15}$  for the adjacent pair of 3.52 Å distant  $\sigma$ 's on (110)-plane of Nickel<sup>9)</sup>;  $i_u$  is now

$$\begin{aligned} i_u &= 2 \times \frac{10^5}{6 \times 10^{23}} \times \frac{1.38 \times 10^{-16} \times T}{6.6 \times 10^{-27}} \times 10^{15} \\ &= 7.0 \times 10^6 T \text{ amp cm}^{-2} \end{aligned} \quad (12.2.b)$$

or  $2 \times 10^9$  at 25°C as referred to in §7.

### § 13. Saturation current

The saturation current  $i_s$  itself is now evaluated according to (12.1) to complete the establishment of the catalytic mechanism.

The  $q_0^{*c}$  or  $q_0^H$  of the second factor of (12.1) is given<sup>4)</sup> as the product of the appropriate vibrational partition function and the BOLTZMANN factor of the energy  $\epsilon_0^{*c}$  or  $\epsilon_0^H$  of the ground state but sufficiently accurately for the present purpose of estimating  $i_s$  by order of magnitude, by the latter factor alone, as

$$-RT \log q_0^{*c} = \epsilon_0^{*c}, \quad -RT \log q_0^H = \epsilon_0^H \quad (13.1. *), (13.1. H)$$

which are exact provided that vibrational frequencies are big enough. We have hence

$$RT \log \frac{q_0^{*c}}{(q_0^H)^2} = -\epsilon_0^{*c} + 2\epsilon_0^H \quad (13.2)$$

The right of (13.2) is determined in what follows referring to recent experimental results of hydrogen adsorption on nickel. The rate  $\bar{v}$  of hydrogen adsorption is given according to (8.1.  $\bar{v}$ ), (11.1. \*) and (2.5.  $\phi$ ), writing  $p^F$  of  $F \equiv H_2$  by (8.5) as  $N^{H_2}/Q^{H_2}$  and replacing  $kTN^{H_2}$  by the partial pressure  $P^{H_2}$  of hydrogen, as

$$\bar{v}_1 = \frac{G_1}{h} \frac{q_0^{*c} P^{H_2}}{Q^{H_2}} (1-\theta)^2 \phi(\theta) \exp\left(-\frac{U^*}{RT}\right) \quad (13.3.a)$$

where  $\bar{v}_1$  is  $\bar{v}$  per unit area. The  $\bar{v}_{1,0}$  i. e.  $\bar{v}$  at extremely small  $\theta$ , where  $U^*$  vanishes, is given according to (3.6.a) as

$$\bar{v}_{1,0} = \frac{G_1}{h} \frac{q_0^{*c}}{Q^{H_2}} P^{H_2} \quad (13.3.b)$$

The rate  $\bar{v}_{1,0}$  on nickel is now known practically<sup>\*)</sup> constant independent of temperature around room temperature. It follows from (13.1. \*)

\*) Cf. ref. 19, p. 71.

and (13.3.b)

$$\left(\frac{\partial \log \bar{v}_{1,0}}{\partial T}\right)_{P^{H_2}} = 0 = \epsilon_0^{*c} - RT^2 \frac{d \log Q^{H_2}}{dT}$$

$RT^2 \frac{d \log Q^{H_2}}{dT}$  equals practically exactly the energy  $\epsilon_0^{H_2}$  of the ground state of hydrogen molecule plus  $\frac{5}{2} RT$ , i. e.

$$RT^2 \frac{d \log Q^{H_2}}{dT} = \epsilon_0^{H_2} + \frac{5}{2} RT \quad (13.4)$$

so that we have

$$\epsilon_0^{*c} = \epsilon_0^{H_2} + \frac{5}{2} RT \quad (13.5)$$

Equating on the other hand  $\bar{v}_1$  of (13.3.a) to  $\bar{v}_1$  of (11.2) for the adsorption equilibrium, we have

$$\frac{kT\theta^2}{(Q_0^{H_2})^2} \exp\left(\frac{2U}{RT}\right) = \frac{P^{H_2}}{Q^{H_2}} (1-\theta)^2$$

and hence for the heat  $H^{H_2}$  of adsorption, according to (13.1.H) and (13.4),

$$H^{H_2} = RT^2 \left(\frac{\partial \log P^{H_2}}{\partial T}\right)_\theta = \epsilon_0^{H_2} + \frac{7}{2} RT - 2\epsilon_0^H - 2U, \quad (13.6)$$

The variation of  $H^{H_2}$  with  $\theta$  must hence be attributed to that of  $2U$  as stated in §5. The value  $H_{\theta=0}^{H_2}$  of  $H^{H_2}$  at  $\theta=0$  is now

$$H_{\theta=0}^{H_2} = \epsilon_0^{H_2} + \frac{7}{2} RT - 2\epsilon_0^H \quad (13.7)$$

KWAN\*) found  $H_{\theta=0}^{H_2}$  at 26 Kcal at 300°C. Hence we have

$$\epsilon_0^{H_2} - 2\epsilon_0^H = 26 \text{ Kcal} - \frac{7}{2} RT = 22 \text{ Kcal} \quad (13.8)$$

substituting the corresponding absolute temperature of the latter observation for  $T$ , and combining (13.8) with (13.5),

$$\epsilon_0^{*c} - 2\epsilon_0^H = 22 \text{ Kcal} + \frac{5}{2} RT = 23.5 \text{ Kcal} \quad (13.9)$$

putting for  $T$  in the latter case that of room temperature appropriate

\*) Cf. ref. (19), p. 89.

to the observation basic to (13.5). The factor  $q_0^{*c}/(q_0^H)^2$  is now determined by (13.2) and (13.9).

The third factor  $\exp\left(\frac{2u - u_1 - u^*}{RT}\right)$  of (12.1) is given, according to (5.7) and (5.8), as

$$\exp\left(\frac{2u - u_1 - u^*}{RT}\right) = \exp\left(\frac{13.9}{RT}\right) \quad (13.10)$$

We have now from (12.1), (12.2), (13.2), (13.9) and (13.10)

$$i_s = 7.0 \times 10^6 T \cdot \exp\left(-\frac{23.5 \text{ Kcal}}{RT}\right) \cdot \exp\left(\frac{13.9 \text{ Kcal}}{RT}\right) \quad (13.11)$$

and in particular,

$$i_s = 2 \times 10^2 \text{ amp cm}^{-2} \quad \text{at } 25^\circ\text{C}$$

or 
$$i_s = 7 \times 10^2 \text{ amp cm}^{-2} \quad \text{at } 50^\circ\text{C}$$

The former value of  $i_s$  is in conformity with the observation of BOCKRIS and AZZAM<sup>10)</sup> that the cathodic current begins at  $10^1 \text{ amp cm}^{-2}$  to approach a saturation value, whereas the latter agrees in order of magnitude with the revised value, given in §5, of the original estimation of OHH<sup>4)</sup> from different basis, amplifying the argument against the criticism of LUKOWZEW, LEVINA and FRUMKIN<sup>22)</sup> referred to there.

It is predicted from (13.11) that the "activation energy",  $RT^2 \frac{d \log i_s}{dT}$  will be *ca.* 10 Kcal.

#### § 14. Conclusive Remark

It has so far been shown that the claims against the catalytic mechanism, that it lead to the value 2 of the TAFEL's constant  $\alpha$ <sup>(6)(7)(17)</sup> in contradiction with the observed *ca.* 0.5 and to an upper bound to the saturation current  $\sim 1 \text{ amp cm}^{-2}$ <sup>10)</sup> inconsistently smaller than the observed value  $> 10^1 \text{ amp cm}^{-2}$ <sup>10)</sup>, originate from fundamental fallacies of ignoring  $f^*$  and of misapplying  $\Delta G_0$  in the rate expression, resulting in a treatment of the heterogeneous reaction of the catalytic mechanism not essentially different from that of TAFEL<sup>1)</sup>, whereas the generalized theory<sup>4),12)-16)</sup> provides a sound basis for unambiguous treatments leading to conclusions from the catalytic mechanism in concordance with experiments in both the above respects.

Another claim against the catalytic mechanism, put forward by BOCKRIS and POTTER<sup>21)</sup> that  $\nu(r)$  be 2 instead of 1 relevant to the catalytic mechanism as determined previously from experiments by HORIUTI<sup>23)</sup>, was shown by HORIUTI and SUGAWARA<sup>9)</sup> invalid on account of the contradiction of the above conclusion of  $\nu(r)=2$  with the assumption of the exclusive linearity of  $\log i$  to  $\eta$  trusted on in arriving at the conclusion itself.

It seems no grounded and definite argument against the catalytic mechanism on nickel hydrogen electrode to exist.

### Summary

1. In order to develop current fallacies in the treatment of heterogeneous reaction, it was first pointed out in terminology of GLASSTONE, LAIDLER and EYRING (GLE)<sup>(6)(7)</sup>, the importance of an exact conception and formulation of the activity coefficient  $f^*$  of the activated complex and of the standard activation free energy  $\Delta G_0$  in the rate expression.
2. The negligence of  $f^*$  was shown to lead to an erroneous conclusion from the catalytic mechanism that TAFEL's constant,  $\alpha = -\frac{RT}{F} \frac{\partial \log i_c}{\partial \eta}$  be 2 exclusively instead of observed value *ca.* 0.5, where  $i_c$  is the cathodic current density,  $-\eta$  the overpotential and  $F$  the Faraday.
3. The misapplication of  $\Delta G_0$  by BOCKRIS and AZZAM<sup>10)</sup> was demonstrated responsible for their erroneous deduction of the upper bound  $\sim 1$  amp  $\text{cm}^{-2}$  to the saturation current density of the catalytic mechanism inconsistently smaller than the observed current density  $> 10^1$  amp  $\text{cm}^{-2}$ .
4. The GLE's method was concluded, when applied to heterogeneous reaction, to be short of predicting the absolute rate, besides associated with such misleading ambiguities as exhibited in 2. or 3. and recourse was necessarily had to the theory of reaction rate generalized by HORIUTI et al.<sup>4), 12)-16)</sup>, formulating  $f^*$  and  $\Delta G_0$  of heterogeneous reaction exactly on its basis in compliance with the requirement of 1.
5. The generalized theory of 4. was shown to lead to  $\alpha$  of *ca.* 0.5 and to the absolute value of the saturation current density  $2 \times 10^3$  amp  $\text{cm}^{-2}$  or its upper bound  $2 \times 10^9$  amp  $\text{cm}^{-2}$  respectively in accordance with experimental results and further to a prediction of the "activation energy"  $RT^2 \frac{d \log i_s}{dT}$  of the saturation current density  $i_s$  at *ca.* 10 Kcal.

### References

- 1) TAFEL, *Z. physik. Chem.* **50**, 641 (1905).
- 2) HABER and RUSS, *Z. physik. Chem.* **32**, 193 (1900); **44**, 641 (1903); **47**, 257 (1904).
- 3) BONHOEFFER, *Z. physik. Chem.* **113**, 199 (1924).
- 4) OKAMOTO, HORIUTI and HIROTA, *Sci. Papers Inst. Phys. Chem. Res. Tokio* **29**, 223 (1936).
- 5) BRÖNSTED, *Z. physik. Chem.* **102**, 169 (1922); *ibid.* **115**, 337 (1925); *Chem. Rev.* **5**, 231 (1928).
- 6) EYRING, LAIDLER and GLASSTONE, *J. Chem. Phys.* **7**, 1053 (1939).
- 7) GLASSTONE, LAIDLER and EYRING, "The Theory of Rate Process", New York, 1941.
- 8) HICKLING and SALT, *Trans. Faraday Soc.* **38**, 474 (1942).
- 9) HORIUTI and SUGAWARA, this volume, p. 1.
- 10) BOCKRIS and AZZAM, *Trans. Faraday Soc.* **48**, 145 (1952).
- 11) EYRING, *J. Chem. Phys.* **3**, 492 (1935).
- 12) HORIUTI, *Bull. Chem. Soc. Japan* **13**, 210 (1938).
- 13) HIROTA and HORIUTI, *Sci. Papers Inst. Phys. Chem. Res. Tokio* **34**, 1174 (1938).
- 14) HORIUTI, "The Theory of Reaction Rate" (in Japanese), Iwanami Series "Physics" X. C. 2, Iwanami Book Company, Tokio, 1940.
- 15) HORIUTI, *J. Res. Inst. Catalysis, Hokkaido Univ.* **1**, 8 (1948).
- 16) HORIUTI, "The Hydrogen Electrode Reaction" (in Japanese), "Experimental Chemistry Series, Part I, 3, Kawade Book Company, Tokio, 1950.
- 17) PARSONS, *Trans. Faraday Soc.* **47**, 1332 (1951).
- 18) KWAN, *J. Res. Inst. Catalysis, Hokkaido Univ.* **1**, 81 (1949).
- 19) KWAN, "Advance in Catalysis", Academic Press Inc., New York, **6**, 67 (1954).
- 20) BOWDEN and RIDEAL, *Proc. Roy. Soc.* **120**, 80 (1928).
- 21) BOCKRIS and POTTER, *J. Chem. Phys.* **20**, 614 (1952).
- 22) LUKOWZEW, LEVINA and FRUMKIN, *Acta Physicochim.* **11**, 21 (1939).
- 23) HORIUTI, *Sci. Papers Inst. Phys. Chem. Res. Tokio* **37**, 274 (1940).
- 24) HORIUTI and IKUSIMA, *Proc. Imp. Acad. Tokio* **15**, 39 (1939).
- 25) ENOMOTO and HORIUTI, *Proc. Japan Acad.* **28**, 493, 499 (1952); *ibid* **29**, 164 (1953); *J. Res. Inst. Catalysis, Hokkaido Univ.* **2**, 87 (1953). HORIUTI, *Proc. Japan Acad.* **29**, 160 (1953).