



Title	ON THE CATALYTIC MECHANISM OF HYDROGEN ELCTRODE REACTION
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 11(3), 164-173
Issue Date	1964-02
Doc URL	http://hdl.handle.net/2115/24769
Type	bulletin (article)
File Information	11(3)_P164-173.pdf



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ON THE CATALYTIC MECHANISM OF HYDROGEN ELECTRODE REACTION

By

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(Received October 4, 1963)

Summary

The catalytic mechanism of hydrogen electrode reaction led, in terms of classical kinetics, to the value 2 of TAFEL constant $\tau = (RT/F) \partial \ln i / \partial \eta$ instead of *ca.* 0.5 as observed, where i is the cathodic current density, η the overvoltage and F the Faraday. OKAMOTO, HORIUTI and HIROTA⁴⁾ deduced τ near 0.5 from the same mechanism with special reference to hydrogen electrode of nickel by means of the generalized statistical mechanical theory^{4,5)} of reaction rate, taking into account the quantum-mechanical exchange repulsions between hydrogen atoms, either adsorbed or implied in the critical complex of the rate-determining step of the catalytic mechanism, *i.e.* the recombination of hydrogen adatoms on the electrode formed by neutralization of hydrogen ions. The τ thus obtained included, as one of its factors, the probability $\Theta_{\sigma^*(0)}$ that the seat σ^* of the critical complex consisting of adjacent pair of sites of adatoms was left free to accommodate the critical complex. The latter authors⁴⁾ identified $\Theta_{\sigma^*(0)}$ with the square of the probability that a single site of adatom was unoccupied, which was only approximate, insofar as adatoms on the adjacent, constituent sites of σ^* exerted repulsion upon each other. The present author⁹⁾ has previously formulated $\Theta_{\sigma^*(0)}$, taking the latter repulsion into account, hence deduced τ -value and the appropriate range of η in much closer agreement with experiment on the one hand and predicted the magnitude of saturation value of i at higher η and its temperature coefficient on the other hand.

In the present article the approximation in the formulation of $\Theta_{\sigma^*(0)}$ is improved. It is thus shown that the appropriate value of τ keeps remarkably constant over a range of η in accordance with experiment as compared with by the previous approximation⁹⁾, whereas the saturation value of i and its temperature coefficient, predicted in the preceding work⁹⁾, remain valid as they stand.

Introduction

The TAFEL law¹⁾

$$\tau \equiv \frac{RT}{F} \frac{\partial \ln i}{\partial \eta} \doteq 0.5 \quad (1)$$

is an important feature of hydrogen electrode reaction, where i is the cathodic current density, η the overvoltage^{*)}, F the Faraday, and RT is of usual

*) The η is here the cathodic polarization or the negative of the potential of the test electrode referred to a reversible hydrogen electrode in the same environment.

meaning. TAFEL¹⁾ himself tried to account for his law on the basis of the catalytic mechanism of hydrogen electrode reaction, hence admitting that the rate was governed by the recombination of hydrogen atoms H(a) on the electrode, *i. e.*



He resorted, in his time, of course, to the classical kinetics in deriving τ from the catalytic mechanism, which led to its value 2 instead of the observed one *ca.* 0.5. This result appears to have ever since been taken as a decisive ground to exclude the catalytic mechanism²⁾, notwithstanding the striking evidence for it as advanced by BONHOEFFER in 1924³⁾.

OKAMOTO, HORIUTI and HIROTA^{4,5)} have generalized the statistical mechanical theory of reaction rate formulated by EYRING and EVANS and POLANYI⁶⁾ in order to deal with the rate of the heterogenous reaction precisely; the generalized theory enabled them to formulate i by taking into account the interactions between hydrogen adatoms H(a)'s and between the latter and the critical complex of the rate-determining step (2). The allowance for the interaction has been required by the following model, on which they have based their theoretical treatment; each metal atom on a lattice plane on the electrode surface provides one of physically identical sites of hydrogen adatoms and an adjacent pair of these sites constitutes a seat σ^* of the critical complex of (2). They have thus calculated i assigning adjacent pairs of sites of different distances on different lattice planes to σ^* and concluded that the predominant contribution to i is made, at least at not very heavy coverage, by such σ^* 's as consisting each of second nearest pair of σ 's, *i. e.* those 3.52 Å apart from each other on (110)-lattice plane of f.c.c. nickel crystal. They thus deduced from the catalytic mechanism that τ remained tolerably a constant proper fraction for a certain range of η in accordance with experiments. It may be noted that evidences have ever since been accumulated for the above model of the sites of adsorption and the existence of considerable repulsive interactions^{7,8,*).}

*) TOYA has deduced from first principles of quantum-mechanics that there exist two sorts of hydrogen adatoms, *i. e.* the r- and s-adatoms⁹⁾; the r-adatom is the adatom of usual sense, while the s-adatom is a sort of hydrogen atom dissolved in the metal, which is situated inside the electronic surface close to it. According to TOYA r-adatoms repulse each other stronger⁹⁾ than estimated by OKAMOTO, HORIUTI and HIROTA as quantum-mechanical exchange repulsion between unbonded hydrogen atoms⁴⁾. The r-adatoms may hence play the part of what we have simply called adatoms in the rate-determining step (2), but its alternative occurrence with s-adatoms might be excluded, inasmuch as the appropriate critical complex imbedded in electron cloud of metal appears to be associated with inhibitive high an activation energy. Adatoms in the text thus are to be understood as r-adatoms.

Their expression⁴⁾ of i thus derived includes as one of its factors the probability $\Theta_{\sigma^*(0)}$ that σ^* is altogether unoccupied. They identified, however, the $\Theta_{\sigma^*(0)}$ with $(1-\theta)^2$, where θ is the probability of a site σ being occupied by an adatom, hence $1-\theta$ that of the site being unoccupied. This is only approximate, since the probability of a σ being unoccupied should depend on whether the adjacent one is occupied or not, insofar as adatoms repulse each other.

The present author has later deduced $\Theta_{\sigma^*(0)}$ ⁹⁾ by taking the repulsion between adjacent adatoms in σ^* into account as

$$\Theta_{\sigma^*(0)} = (1-\theta')(1-\theta) = (1-\theta)^2 \varphi(\theta), \quad (3. a)$$

where

$$\varphi(\theta) = \left[1 + \theta \left\{ \exp\left(\frac{u_1\theta}{RT}\right) - 1 \right\} \right]^{-1}; \quad (3. b)$$

θ' is the probability that one of the constituent σ' s of the σ^* , denoted by σ_1 , is occupied, while the other, σ_2 , is kept vacant, and u_1 is the repulsive potential between the two adatoms occupying σ_1 and σ_2 . On the basis of the above equations the TAFEL law has been derived⁹⁾ in much closer agreement with experimental result than in the previous work⁴⁾, and the magnitudes of the saturation current density and of its temperature coefficient have been predicted⁹⁾.

The factor $(1-\theta)$ in the second member of (3.a) is now the probability that the σ_2 is unoccupied whether the σ_1 is occupied or not, which has been calculated by assuming that the repulsive potential of the adatom on σ_2 due to that on σ_1 is proportional to θ or by smearing the latter adatom together with other adatoms around the former. The factor $(1-\theta')$ has been deduced on the other hand for the definite vacance of σ_2 . The repulsion exerted by an adatom on σ_1 upon that on σ_2 is thus taken into account by an approximation different from the repulsion reciprocally exerted by an adatom on σ_2 upon that on σ_1 . It is desirable to deal consistently equally with them.

The present article is concerned with the formulation of $\Theta_{\sigma^*(0)}$ improved in this regard and with the revision of the relevant numerical results and arguments in the previous paper⁹⁾.

§ 1. Formulation of $\Theta_{\sigma^*(0)}$

The formulation of $\Theta_{\sigma^*(0)}$ is revised as mentioned in the introduction on the basis of the same models of adsorbent and the rate-determining step (2), and of the same law of repulsion as those underlying the previous work⁹⁾.

The $\Theta_{\sigma^*(0)}$ is expressed in general as

$$\Theta_{\sigma^*(0)} = \Sigma C_{\sigma^*(0)} / \Sigma C \quad (4)$$

in terms of partition functions $\Omega C_{\sigma^*(0)}$ and ΩC respectively of $C_{\sigma^*(0)}$ and C , where $C_{\sigma^*(0)}$ is the whole assembly in question with the specification that a definite σ^* on the electrode is unoccupied with certainty and C is the same assembly but without any such specification. The all possible states of C are, with special reference to the σ^* , $C(I)$, $C(II)$ and $C(III)$, where the σ^* is occupied by none, by only one adatom and by two ones respectively. The partition function $\Omega C(I)$ of $C(I)$ is $\Omega C_{\sigma^*(0)}$ itself, *i. e.*

$$\Omega C(I) = \Omega C_{\sigma^*(0)}. \quad (5. I)$$

The $C(II)$ is derived from $C_{\sigma^*(0)}$ by extracting an adatom from outside the σ^* and putting the extracted one on either of the constituent σ 's of the σ^* . The free energy of the assembly decreases by the extraction from $-kT \ln \Omega C_{\sigma^*(0)}$ by the chemical potential $\mu^H = -kT \ln p^H$ assigned to a single atom, where k is the BOLTZMANN constant and p^H is the appropriate factor of multiplication of the partition function. By putting the extracted adatom in a definite constituent site of the unoccupied σ^* , the free energy increases by the work $-kT \ln q^H$ required to transfer an adatom from its standard state to the site. The latter work is expressed as $-kT \ln q^H = -kT \ln q_0^H + (u - u_1)\theta$, where $-kT \ln q_0^H$ is the particular value of $-kT \ln q^H$ in the absence of environing adatoms and $(u - u_1)\theta$ is the additional work due to the repulsion exerted by the latter, which is approximated by the appropriate potential assumed to be proportional to θ with the constant of proportion $u - u_1$, *i. e.* the repulsive potential u at full occupation of the environing sites less that u_1 due to an adatom on the other constituent site of the σ^* , which is vacant with certainty in this case. The free energy of the resultant assembly is now $-kT \ln \Omega C_{\sigma^*(0)}$ plus the above increments, *i. e.* $-kT \ln \Omega C_{\sigma^*(0)} + kT \ln p^H - kT \ln q_0^H + (u - u_1)\theta$, its BOLTZMANN factor being the appropriate partition function, *i. e.* $\Omega C_{\sigma^*(0)} q_0^H \exp \{ -(u - u_1)\theta/kT \} / p^H$. The partition function $\Omega C(II)$ of $C(II)$ is the sum of the two identical partition functions respectively appropriate to one of the two physically identical constituent sites of the σ^* to be occupied, *i. e.*

$$\Omega C(II) = 2 \Omega C_{\sigma^*(0)} \left[q_0^H \exp \left\{ -(u - u_1)\theta/kT \right\} / p^H \right]. \quad (5. II)$$

The $C(III)$ is derived from $C(I)$, *i. e.* $C_{\sigma^*(0)}$ by extracting two adatoms from outside the σ^* and putting them in it. The free energy $-kT \ln \Omega C_{\sigma^*(0)}$ of $C(I)$ decreases by the extraction twice as much as that in case of a single adatom extracted, *i. e.* by $2\mu^H = -2kT \ln p^H$ and increases by putting them in the σ^* by $-2kT \ln q_0^H + 2(u - u_1)\theta + u_1$, where $-2kT \ln q_0^H + 2(u - u_1)\theta$ is twice the above formulated work required to transfer an adatom from its standard state to a definite site in the σ^* and the last term u_1 is the additional work required

to overcome the mutual repulsion between the two adatoms transferred. The free energy $-kT \ln \Omega C(\text{III})$ of the resultant assembly is $-kT \ln \Omega C_{\sigma^*(0)}$ plus the increment, *i. e.* $-kT \ln \Omega C_{\sigma^*(0)} + 2kT \ln p^H - 2kT \ln q_0^H + 2(u - u_1)\theta + u_1$, hence its BOLTZMANN factor $\Omega C(\text{III})$, *i. e.*

$$\Omega C(\text{III}) = \Omega C_{\sigma^*(0)} \left[q_0^H \exp \left\{ -(u - u_1)\theta / kT \right\} / p^H \right]^2 \exp(-u_1/kT). \quad (5. \text{III})$$

The ΩC is now the sum of $\Omega C(\text{I})$, $\Omega C(\text{II})$ and $\Omega C(\text{III})$ given by the above equations, *i. e.*

$$\Omega C = \Omega C_{\sigma^*(0)} (1 + 2\beta + \xi\beta^2), \quad (6. \text{a})$$

where

$$\beta = q_0^H \exp \left\{ -(u - u_1)\theta / RT \right\} / p^H \quad (6. \text{b})$$

and

$$\xi = \exp(-u_1/RT); \quad (6. \text{c})$$

u and u_1 are respectively referred to one mol adatom in (6) in line with (3) given in the previous work⁹⁾.

We have now from (4) and (6. a)

$$\Theta_{\sigma^*(0)} = (1 + 2\beta + \xi\beta^2)^{-1}. \quad (7. \text{a})$$

The $\varphi(\theta)$ is defined in line with (3), as

$$\varphi(\theta) = (1 - \theta)^{-2} (1 + 2\beta + \xi\beta^2)^{-1}. \quad (7. \text{b})$$

§ 2. Formulation of θ

Our application of (7) requires yet the formulation of θ in terms of β and ξ . We see from the above derivation that the partition function $\Omega C_{\sigma(\text{H})}$ of the assembly $C_{\sigma(\text{H})}$, where a definite one, say σ_1 , of the two constituent sites of the σ^* is occupied, is expressed by the sum of $\Omega C(\text{II})/2$ and $\Omega C(\text{III})$, which correspond respectively to the two possible states of $C_{\sigma(\text{H})}$, *i. e.* those associated with vacancy and occupancy of σ_2 . We have hence from (5. II) and (5. III) with reference to (6. b) and (6. c)

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

The θ is now the ratio of $\Omega C_{\sigma(\text{H})}$ to ΩC , hence according to the above equation and (6. a)

$$\theta = \beta(1 + \xi\beta) / (1 + 2\beta + \xi\beta^2), \quad (8. \text{a})$$

from which it follows immediately that

$$1 - \theta = (1 + \beta) / (1 + 2\beta + \xi\beta^2) \quad (8. \text{b})$$

and

$$\theta/(1-\theta) = \beta(1 + \xi\beta)/(1 + \beta). \quad (8. c)$$

The $\Theta_{\sigma^*(0)}$ and θ are thus formulated consistently by dealing equally with the two constituent sites of σ^* as (7.a) and (8).

In the previous paper θ' in (3.a) has been derived taking the absence of the neighbouring adatom in the same σ^* discretely into account in accordance with the present approximation, but the θ there has not, as mentioned in the introduction. Eq. (8) gives now the θ in accordance with the present approximation. It is hence shown as below that $1-\theta'$ in the previous paper⁹⁾ and $1-\theta$ of (8) give (7.a) consistently according to (3.a). The θ' is given by the two equations derived toward the end of §9 of the previous paper⁹⁾, *i.e.*

$$p^H = \frac{1-\theta'}{\theta'} q^{H'}, \quad q^{H'} = q_0^H \exp\left(-\frac{u'\theta}{RT}\right),$$

where u' is according to Eq. (3.3) in the previous paper⁹⁾

$$u' = u - u_1,$$

and p^H , q_0^H , u and u_1 are respectively of the same meanings as those in the present paper. Eliminating $q^{H'}$ and u' from the above three equations, we have

$$p^H = \frac{1-\theta'}{\theta'} q_0^H \exp\left\{-\frac{(u-u_1)\theta}{RT}\right\}$$

or referring to (6. b),

$$1-\theta' = 1/(1+\beta),$$

which reproduces (7.a) as combined with (8. b) accordings to (3.a).

§ 3. $r(\theta) \equiv \partial \ln \varphi(\theta) / \partial \theta$

The present revision of $\Theta_{\sigma^*(0)}$ makes difference in τ , if at all, through $r(\theta) \equiv \partial \ln \varphi(\theta) / \partial \theta$ in the equation

$$\tau = \frac{2u - u^* + 2RT/\theta + RT\gamma(\theta)}{u + RT/\theta(1-\theta)}, \quad (9)$$

which has been derived in the previous work⁹⁾ and holds formally as well for the present approximation, where u^* is the repulsive potential of the critical complex at $\theta=1$. The $r(\theta)$ is derived from (7. b) as*

*) We have from (7. b)

$$r(\theta) \equiv \partial \ln \varphi(\theta) / \partial \theta = 2\varphi(\theta)(1-\theta) \left\{ 1 + 2\beta + \xi\beta^2 - (1-\theta)(1 + \beta\xi) \partial \beta / \partial \theta \right\},$$

where $\partial \beta / \partial \theta$ is obtained by differentiation of (8. c) as

$$\frac{\partial \beta}{\partial \theta} = \frac{\beta(1+\beta)(1+\xi\beta)}{\theta(1-\theta)(1+2\xi\beta+\xi\beta^2)}.$$

On substitution, we have

$$r(\theta) = 2\varphi(\theta)(1-\theta) \left\{ 1 + 2\beta + \xi\beta^2 - \frac{\beta(1+\beta)(1+\xi\beta)^2}{\theta(1+2\xi\beta+\xi\beta^2)} \right\}.$$

Eq. (10) is arrived at by replacing $1+2\beta+\xi\beta^2$ for the factor $\beta(1+\xi\beta)/\theta$ in the second term in the parentheses $\{ \}$ according to (8.a) and substituting $\varphi(\theta)$ from (7. b).

$$\gamma(\theta) = -\frac{2\beta(1-\xi)}{(1-\theta)(1+2\xi\beta+\xi\beta^2)} \quad (10)$$

Eq. (10) shows that $\gamma(\theta)$ is essentially negative, since β , ξ and $1-\theta$ are all positive and ξ is less than unity according to (6.c) because of the positive repulsive potential u_1 , *i. e.*

$$\gamma(\theta) < 0. \quad (11)$$

§ 4. Numerical Results

It follows from (8.c), noting both β and ξ are positive by definition, that $\beta=0$ or $\beta \rightarrow \infty$ according as $\theta=0$ or $\theta \rightarrow 1$ and in consequence from (7.b)*)

$$\varphi(0) = 1, \quad \varphi(1) = \xi; \quad (12. a), (12. b)$$

which are in coincidence with those derived from (3.b).

We have on the other hand from (10)**)

$$\gamma(0) = 0, \quad \gamma(1) = 2(\xi-1), \quad (13. a), (13. b)$$

which contrast with those obtained from (3.b), *i. e.*

$$\gamma(0) = 0, \quad \gamma(1) = \xi - 1 - u_1/RT.$$

TABLE 1. Revised Values of $\varphi(\theta)$, $\gamma(\theta)$ and $2u-u^*$ and the Lower Bound $-2(1/\theta+u_1/RT)$ to $\gamma(\theta)$ ***)
 $u=25$ Kcal, $u_1=1.38$ Kcal, $\tau=0.52$, 25°C .

θ	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\varphi(\theta)$	0.989	0.947	0.854	0.690	0.476	0.303	0.205	0.151	0.119
$-\gamma(\theta)$	0.241	0.674	1.477	2.895	4.409	4.343	3.445	2.694	2.171
$2\left(\frac{1}{\theta} + \frac{u_1}{RT}\right)$	24.66	14.66	11.32	9.66	8.66	7.99	7.51	7.16	6.88
$2u-u^*$ Kcal	4.72	9.40	11.39	13.04	14.47	14.88	14.82	15.04	16.39

*) We have from (8.c) $\lim_{\theta \rightarrow 1} \beta(1-\theta) = \lim_{\theta \rightarrow 1} \theta \frac{1+\beta}{1+\xi\beta} = \xi^{-1}$, hence from (7.b)

$$\varphi(1) = \lim_{\theta \rightarrow 1} \{(1-\theta)^2 + 2(1-\theta)^2\beta + \xi(1-\theta)^2\beta^2\}^{-1} = \xi.$$

**) The $\gamma(1)$ is evaluated by writing (10) in the form

$$\gamma(\theta) = 2(\xi-1)\{(1-\theta)/\beta + 2\xi(1-\theta) + \xi(1-\theta)\beta\}^{-1}$$

and noting that $\lim_{\theta \rightarrow 1} \beta(1-\theta) = \xi^{-1}$ as shown in the above footnote *).

***) This contrasts with the Table on p. 68 in the previous paper⁹⁾, which contains the values of $\varphi(\theta)$, $\gamma(\theta)$ and $2u-u^*$ as based on (3.b). The minus sign of $\gamma(\theta)$ is missing in the latter Table by misprint.

The Table 1 shows the revised values of $\varphi(\theta)$ and $\gamma(\theta)$ at 25°C calculated respectively by (7.b) and (10) with reference to (8) and (6.c) at different values of θ , as well as the values of $2u-u^*$ reversely calculated by (9) on the base of the revised equation of $\gamma(\theta)$ from the same fundamental values, *i. e.* $u=25$ Kcal, $u_1=1.38$ Kcal and $\tau=0.52$. The present revision makes some difference in the numerical results as seen in the Table in comparison with the previous one⁹⁾. It may be noted that the values of $2u-u^*$ reversely calculated from the constant value of τ , keeps appreciably constant for $\theta>0.5$ as compared with in the previous case⁹⁾, which means that τ remains more precisely constant for *ca.* 0.4 volt range^{*1)} of η .

The saturation current density and its temperature coefficient evaluated in the previous work⁹⁾ hold good just as they stand even on the basis of the present approximation, because $\varphi(\theta)$ is the only factor in i which is liable to alteration along with the revision, but not at $\theta=1$ particularly as seen in (12.b), where the current density attains its saturation value according to the catalytic mechanism.

§ 5. Positive Proper Fraction of τ

Arguments were advanced in the previous paper⁹⁾ verifying that τ remained a positive proper fraction for $\theta>0.5$ according to the theory of catalytic mechanism^{**1)}. It is now shown below that the similar arguments apply with some alteration on the basis of the present approximation.

We have, as shown in the previous paper⁹⁾,

$$u < u^* < 2u - 2u_1, \quad (14)$$

which holds good irrespective of the approximation. It follows from the above inequities by subtracting $2u$ from all the members and inverting their signs, that

*) The range of η over which τ stays nearly constant is calculated as follows. The chemical potential μ^H of adatom assigned to one mol is expressed as $-RT \ln p^H$ as stated in §1 on the one hand and as $\mu^H = \mu_1^H + F\eta$ according to Eqs. (4.1.H) and (4.2) in Ref. (9) on the other hand, where μ_1^H is the value of μ^H at $\eta=0$ and the sign of η is reversed from that in the previous paper⁹⁾. [*cf.* footnote *) on p. 164]. It follows that $F\eta = RT \ln (q_0^H/p^H) + \text{constant}$, inasmuch as q_0^H is a constant at constant temperature [*cf.* §1]. Eqs. (6.b) and (8) determine now the value of q_0^H/p^H as a function of θ . The range of η is calculated by the equation, $F\eta = RT \ln q_0^H/p^H + \text{constant}$, from the values of q_0^H/p^H at $\theta = \text{ca. } 0.5$ and *ca.* 0.8.

**) The arguments have been presented for $\theta>0.6$ in the previous paper⁹⁾, but found later to hold good as they are for $\theta>0.5$.

$$u > 2u - u^* > 0, \quad (15)$$

inasmuch as u_1 is positive. The term $2RT/\theta$ in (9) is now positive and smaller than $RT/\{\theta(1-\theta)\}$ for $\theta > 0.5$. It follows that, by crossing out the term $RT\gamma(\theta)$ in (9), its right-hand side becomes a positive proper fraction as well as an upper bound to τ according to (11) and (15), *i. e.*

$$\tau < \frac{2u - u^* + 2RT/\theta}{u + RT/\{\theta(1-\theta)\}}. \quad (16. a)$$

We see on the other hand in Table 1

$$\gamma(\theta) > -2/\theta - 2u_1/RT.$$

Substituting the right-hand side of the above inequality for $\gamma(\theta)$ in (9), we have

$$\tau > \frac{2u - u^* - 2u_1}{u + RT/\{\theta(1-\theta)\}}. \quad (16. b)$$

The numerator of the right-hand side of (16.b) is positive according to the second inequality of (14), but less than u by the first inequality of (15). Since $RT/\theta(1-\theta)$ in the denominator of (16.b) is positive, the right-hand side of (16.b) is a positive proper fraction. It follows that τ is a positive proper fraction for $\theta > 0.5$, where τ lies between the two positive proper fractions according to (16).

§ 6. Conclusion

The approximation of $\varphi(\theta)$ has been improved from (3.b) used in the previous paper⁹⁾ to (7.b) in the present one and the numerical results obtained and the arguments advanced in the previous paper⁹⁾ have been revised on the base of (7.b). The theoretical value of τ has been found more closely kept constant for $\theta > 0.5$ according to the revised $\varphi(\theta)$.

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