Quantum Electrochemistry: New Aspects in Electrochemistry and Electrocatalysis

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ABSTRACT
Quantum mechanical theory of electrochemical kinetics based on Fermi’s golden rule was formulated by introducing the concept of electron transfer distance. The expressions for the exchange current density and standard rate constant in electrochemistry were derived in analytical form, as well as exponential current overpotential dependence. The theory corresponds well to the electrode kinetics based on the transition state theory. It was applied to various kinds of electrode reactions to analyze the standard rate constants and the exchange current densities reported in past literature. The evaluated magnitudes of the electron exchange energy were very small, being in the order of $10^{-3}$ eV–$10^{-5}$ eV. A new theory of transfer coefficient was constructed based on Debye-Hückel theory for electrolyte solutions could explain quantitatively the dependence of the transfer coefficient on the ionic strength of electrolyte solutions. It was demonstrated that the transfer coefficient represents electrostatic screening of the electrode potential by ions near the electrode and its magnitude was calculated quantitatively. Electron transfer distance was obtained by analyzing the dependence of the transfer coefficient on the ionic strength of electrolyte solutions. Our theory supported the ordinary electron transfer mechanism due to the overlap of wave functions between the electrode and redox species, denying tunneling mechanism.

Keywords : Quantum Electrochemistry, Electron Transfer Distance, Quantum Mechanical Nernst Equation, New Interpretation of Transfer Coefficient

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1. Introduction

Electrode reaction is based on the electron transfer at the electrode-electrolyte interface. These two or three decades the theory and experiments have made remarkable progress on the inter-molecular electron transfer. We could say that the problems of inter-molecular electron transfer have now been almost solved.

On the other hand, microscopic investigation of the electrode reaction is still at the early research stage, because of the complicated electron transfer phenomena at the electrode-electrolyte interface. Considering the fact that electron is typical quantum, it is beyond dispute that the electrode reaction should be described based on the quantum theory, to clarify the essential mechanism.

Most successful theory of electrochemistry at present is based on the transition state theory. Since this theory can explain qualitatively various electrochemical phenomena such as potential dependence of the current, it is still used among electrochemists.

Since this theory is a phenomenological theory based on the transition state theory, it cannot explain electron transfer at the electrode-electrolyte interface at microscopic level. As for the quantum theory of electrode kinetics, a quantum theory by Dogonatze and Levich et al. (Russian school) is well known. However, their theory cannot explain experimental results such as current potential relation.

We have proposed a quantum mechanical theory of electron transfer reactions at metal electrodes. In this theory the electron transfer rates are expressed based on the time-dependent perturbation theory by Yomosa. In this theory the free electron theory was adopted for the electronic structure of the metal electrodes. The distribution functions in Gerischer’s theory and Hopfield’s theory were used for the distribution functions of redox species in the electrolyte solution near the electrode surface.

The obtained potential dependence of the electron transfer rate in the weak coupling case is of the same form as the Butler-Volmer equation in the classical electrochemistry based on the transition state theory. In a previous manuscript, the theory was improved to interpret the activation energy of the exchange current density and the standard rate constant for cathodic electron transfer. Hydrogen exchange current densities and overpotential of hydrogen evolution were evaluated quantitatively at various metal electrodes by using this improved theory.

Recently, we have proposed a new theory and interpretation of the transfer coefficient based on electrostatic screening that can quantitatively explain the dependence of transfer coefficient on the ionic strength of the electrolyte solution. It was shown that the information on the “electron transfer distance” is contained in the transfer coefficient. In the previous manuscript, we have improved the fundamental equation of electron transfer rate at metal-electrolyte interface based on the Fermi golden rule, by introducing a new parameter of electron transfer distance.

Based on this improved theory, we have derived the quantum mechanical expressions for kinetic parameters of electrode kinetics such as the exchange current density and the standard rate constant in analytical form. We have applied this theory to interpret the physical meanings of the kinetic parameters accumulated in electrochemistry from a quantum mechanical point of view and evaluated the magnitude of electron transfer integral at the electrode/electrolyte interface.
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Our theory corresponds well to the electrochemical theory\(^8\) based on the transition state (Hereafter Let’s call it “classical theory”) to discriminate from quantum theory and explain well experimental results.

Moreover, this theory is easy to understand even for experimentalists if one learns introductory course of quantum mechanics. In this article we would like to account for the outline of our theory and discuss the application to experimental results to show its validity and future aspects in electrochemistry.

2. Fundamental Approach of Quantum Electrochemistry

2.1 Electron transfer distance and transition probability

In electrochemical experiments electrical current is measured to evaluate the kinetic rate. The current which passes through the electrode is expressed for one electron transfer reaction, as

\[
i = eAC
\]

where \(e\), \(A\), and \(C\) represent electron charge, the surface area of the electrode, and the bulk concentration of the redox species, respectively.\(^9\)\(^,\)\(^1\)\(^1\) \(k\) represents the reaction rate of the electrode kinetics. When the volume concentration \([\text{cm}^{-3}]\) is employed for \(C\) in Eq. (1), the dimension of electrochemical reaction rate \(k\) is \([\text{cm}^{-2}\text{s}^{-1}]\).

The current which passes through the electrode surface is also expressed as

\[
i = ewAC_s
\]

Here \(C_s\) represents the concentration of redox species (number of redox species in the unit area) near the electrode surface which are involved in the electrode reaction. \(w\) represents the transition probability of the electron transfer between the electrode-electrolyte interface which is expressed by the following equation, based on Fermi’s golden rule.\(^1\)\(^1\)

\[
w = \frac{2\pi}{\hbar} \int_{-\infty}^{+\infty} D_v(E)D_\epsilon(E)dE
\]

(A-6)

From Eqs. (1) and (2)

\[
kC = wC_s
\]

is obtained. Now let’s consider a new parameter \(r_{et}\), i.e. electron transfer distance for the electron transfer between the electrode-electrolyte interface. The electron transfer distance \(r_{et}\) represents the average distance of the redox species from the electrode surface through which electron transfer takes place.\(^1\)\(^,\)\(^1\)\(^1\) One may doubt whether there exists such a definite electron transfer distance \(r_{et}\) for the electrode reaction.

Electron transfer distance \(r_{et}\) is considered as follows. The concentration of the redox species must be depleted near the electrode surface, because of the steady state electrode reaction. Therefore the distribution of redox species near the electrode surface \(p(r)\) is thought to be drawn as in Fig. 1.

In Figs. 1, 2 and 3 \(r\) represents the distance between the redox species and the compact layer on the electrode surface. For simplicity \(p(r)\) is the distribution vertical to the electrode surface. A compact layer which is composed of water molecules and electrolyte adsorbed on the electrode surface is assumed in the electrochemistry.\(^8\) The thickness of the compact layer \(\delta_c\) is assumed to be approximately 2 Å.\(^1\)\(^5\) The redox species are distributed outside of the compact layer, since they cannot penetrate the compact layer. Thus horizontal \(r\) axis in Fig. 1 represents the distance from the compact layer on the electrode surface.

On the other hand, transition probability of the electron transfer at the electrode surface \(w\) would decrease exponentially as a function of \(r\) as in the case of electron transfer between molecules.\(^1\)\(^\text{9}\) Figure 2 illustrates the situation. Now, let’s consider a function \(g(r) = p(r)w(r)\), i.e., the product of \(p(r)\) and \(w(r)\). The function \(g(r) = p(r)w(r)\) must be proportional to the current due to the electrode reaction.

The function \(g(r)\) is expected to show a maximum value at a certain value \(r = r_0\), as is shown in Fig. 3. Since \(g(r)\) is considered to be proportional to the probability of the electron transfer at \(r\) on the electrode surface, \(r_{et}\) can be given approximately by the following equation.\(^1\)\(^1\)

\[
r_{et} \approx \delta_c + r_0
\]

In the previous manuscript, we showed that the electron transfer distance \(r_{et}\) can be determined experimentally by analyzing the dependence of transfer coefficient on ionic strength.\(^1\)\(^0\)

For the surface concentration \(C_s\), let’s assume

\[
C_s = \gamma Cr_{et}
\]

where \(\gamma\) is a constant. Equation (5) represents the assumption that the surface concentration \(C_s\) is proportional to the bulk concentration \(C\) and electron transfer distance \(r_{et}\).

For \(\gamma > 1\), the surface concentration \(C_s\) is larger than the bulk concentration \(C\).

For \(\gamma = 1\), the surface concentration \(C_s\) is equal to the bulk concentration \(C\).

\[\text{Figure 1. Schematic illustrations of the distribution of redox species } p(r)\]

\[\text{Figure 2. Transition probability } w(r) \text{ of the electron transfer at the electrode surface as a function of } r\]

\[\text{Figure 3. } r \text{ dependence of } g(r) = p(r)w(r)\]
For $\gamma < 1$, the surface concentration $C_s$ is smaller than the bulk concentration $C$.

We define electron transfer time $t_{et}$ by the following equation:

$$t_{et} = \frac{1}{w}$$  \hspace{1cm} (6)

From Eqs. (3), (5) and (6)

$$k = w r_{et} = \gamma \frac{r_{et}}{t_{et}}$$  \hspace{1cm} (7)

is obtained.

Equation (7) shows clearly that the reaction rate $k$ defined by Eq. (1) is proportional to $r_{et}$. $r_{et}$ is thought to be the transition velocity of the electron transfer between the electrode surface and redox species which are located near the electron transfer distance $r_{et}$ from the electrode surface. Its dimension is the same with the velocity, i.e., $[\text{cm s}^{-1}]$. Equation (7) is reasonable, because the electron transfer takes place at the electrode-electrolyte interface. The electrode reaction rate $k$ expressed by Eq. (7) explains well the physical meaning of Eq. (1).

By using Eq. (5), Eq. (2) is written as,

$$i = ewA C_r = ewA C_{r_{et}}$$  \hspace{1cm} (8)

The right hand term $A_{r_{et}}$ of Eq. (8) represents a very thin surface layer of the thickness $r_{et}$ and the area $A$. Since the right hand term $A_{r_{et}}$ represents the number concentration of the thin layer, $ewA C_{r_{et}}$ represents the electric current due to the electrode reaction with transition probability $w$.

From the above consideration, let’s call $A_{r_{et}}$ “Electron transfer layer”.\textsuperscript{11} From Eqs. (A-6) and (7), we can express the electrode reaction rate $k$ as follows.

$$k = w r_{et} = \frac{2 \pi}{h} \gamma r_{et} \int_{-\infty}^{+\infty} D_r(E) D_r(E) dE$$  \hspace{1cm} (9)

Equation (9) represents a quantum mechanical equation of the electrode reaction rate $k$.

Parameter $v$ in Eqs. (A-6) and (9) represents the electron exchange integral as follows,

$$v = \langle \Psi_f | H^{'} | \Psi_i \rangle$$  \hspace{1cm} (A-2)

where $\Psi_f$ and $\Psi_i$ represent the wave function of the final state and the initial state of the redox species for the electron transfer, respectively, and $H^{'}$ represents the interaction Hamiltonian between metal electrode and redox species. This type of integral is called transfer integral in solid state physics. Since the electron exchange integral $v$ is the driving force of the electron transfer, let’s call it electron transfer integral or electron transfer energy in order to emphasize its physical meaning and the role in the electrode kinetics.\textsuperscript{11}

\subsection*{2.2 Cathodic process}

In a previous manuscript, we improved our theory especially for cathodic electron transfer at metal electrode.\textsuperscript{8} Although the obtained results remain almost the same as the original theory,\textsuperscript{8} the physical meaning of the electrode reaction became clearer. In the weak coupling case, where the overlap between the state density of electrons in the metal electrode and the state density of the electron acceptor is weak, the current density-overpotential equation for cathodic reaction is given by\textsuperscript{8,11}

$$i_c = \frac{2 \pi e^2}{h} r_{et} C_r \rho(E_f) \exp \left(-\frac{\Delta F_0}{kT} \right)$$  \hspace{1cm} (11)

In Eq. (11) $\Delta F_0$ represents the activation energy of the exchange current density.\textsuperscript{8,11} The activation energy of the exchange current density is given as follows\textsuperscript{8,11}

$$\Delta F_0 = E_a - \Delta \epsilon_{f_i} + eV_{eq}$$  \hspace{1cm} (12)

In the classical electrochemistry based on the transition state theory, the current density-overpotential equation for cathodic reaction is given by\textsuperscript{8}

$$i_c = i_0 \exp \left(-\frac{\epsilon_{f_i} \eta}{kT} \right)$$  \hspace{1cm} (10-1)

In Eq. (10-1) $\alpha_c$ is called transfer coefficient or symmetric factor.\textsuperscript{8} It is fair to regard transfer coefficient ($\alpha_c$) as the heart of electrode kinetics.\textsuperscript{11}

In the classical electrochemistry based on the transition state theory, transfer coefficient ($\alpha_c$) is considered to indicate the symmetry of the potential barrier of the transition state of the electron transfer at the electrode.\textsuperscript{8} Equation (10) for cathodic reaction in quantum mechanical electrochemistry resembles Eq. (10-1). Parameter $\alpha$ corresponds to transfer coefficient $\alpha_c$ in the classical electrochemistry. By comparing Eq. (10) with Eq. (10-1),

$$\alpha_c = 1 - \alpha$$  \hspace{1cm} (10-2)

holds.\textsuperscript{10}

In the weak coupling case, for the cathodic reaction rate $k_c$,

$$k_c = \frac{2 \pi e^2}{h} r_{et} \rho(E_f) \exp \left(-\frac{E_a - E_f}{kT} \right)$$

$$= \frac{2 \pi e^2}{h} r_{et} \rho(E_f) \exp \left(-\frac{\Delta E_0}{kT} \right)$$  \hspace{1cm} (13)

is obtained.\textsuperscript{11} In Eq. (13) $E_a$ represents the energy level of the electron acceptor near the electrode surface and $E_f$ represents the Fermi level of the metal electrode and $\Delta E_0$ represents the activation energy of the cathodic electron transfer rate $k_c$.\textsuperscript{9,11}

The activation energy of the cathodic electron transfer rate $\Delta E_0$ is defined as

$$\Delta E_0 = E_{eq} - E_f$$  \hspace{1cm} (13-1)

Figure 4 illustrates the physical meaning of the exchange current density $i_c$.

\begin{figure}[h]
  \centering
  \includegraphics[width=0.5\textwidth]{figure4}
  \caption{Physical meaning of the exchange current density $i_c$.}
\end{figure}

\textbf{Figure 4.} Physical meaning of the exchange current density $i_c$. 

At equilibrium, electrode potential is located at $V_{eq}$ since $\eta = 0$. Fermi level $E_f$ is located at $E_f = -eV_{eq}$. Then the energy gap between electron acceptor and Fermi level $E_f$ is

$$\Delta E^0 = E^0_a - \Delta \epsilon_f + eV_{eq},$$

(14)
as is shown in Fig. 4. The exchange current density $j_0$ is the thermal current that flows from the cathode to the electron acceptors near the electrode surface. $\Delta E^0$ defined by Eq. (14) corresponds to the activation energy of the exchange current density $j_0$.

The overpotential $\eta$ and equilibrium potential $V_{eq}$ are defined by Nernst equation as

$$\eta = V - V_{eq},$$

(15)

$$V_{eq} = V_0 + \frac{kT}{e} \ln \frac{C_0}{C_b},$$

(16)

Here $V$, $V_{eq}$ and $V_0$ represent the electrode potential, the equilibrium potential and the standard redox potential, respectively. $C_0$ and $C_b$ represent the concentration of the oxidized and reduced species near the electrode surface, respectively. The definition of the overpotential $\eta$ and the equilibrium potential $V_{eq}$ in Eqs. (14) and (15) is the same as in classical electrochemistry based on the transition state theory.8,19 It is noted that Eq. (10) has the similar form as the cathodic component of Butler-Volmer equation in the classical electrochemistry based on the transition state theory.8,19

### 2.3 Anodic process

For the anodic electron transfer reaction the transition probability of anodic electron transfer rate $w_a$ can be expressed from Eq. (A-6) as,

$$w_a = \frac{2\pi e}{h} v^2 \int_{-\infty}^{+\infty} D_{a}(E)D_{-}(E)dE,$$

(17)

where $D_{a}(E)$ represents the distribution function of the electron-accepting state of the metal electrode and $D_{-}(E)$ represents the distribution function of the electrons in the electron donor $D$ near the electrode surface. $E$ represents the electron energy. In the case of the anodic electron transfer reaction, the metal electrode functions as electron acceptor. When free electron theory is used for the metal electrode, $D_{a}(E)$ is expressed by the state density of unoccupied states (holes) of the metal electrode as,4

$$D_{a}(E) = \rho(E)(1 - f(E)),$$

(18)

where $\rho(E)$ and $f(E)$ represent the state density of electrons in the metal electrode and Fermi Dirac distribution function, respectively.4

In the case of $E_f - E \geq 4kT$, $D_{a}(E)$ of Eq. (18) is well approximated by Boltzmann distribution as4,11

$$D_{a}(E) = \rho(E) \exp \left( - \frac{E_f - E}{kT} \right),$$

(19)

Where $E_f$ represents the Fermi level of the metal electrode.

As for the distribution function of the electrons in the electron donors $D_{-}(E)$, we used the following distribution function in the previous manuscript3 that was introduced by Gerischer and Hopfield.6,7

$$D_{-}(E) = \frac{1}{\sqrt{4\pi kT}} \exp \left( - \frac{(E - E_0 + \lambda)^2}{4kT} \right),$$

(20)

where $E_0$ represents the energy level that corresponds to the redox potential of $D^+/D$ which is approximately equal to the energy level of the electron donor $D$ and $\lambda$ represents the reorganization energy.

Substitution of Eqs. (19) and (20) into Eq. (17) yields

$$w_a = \frac{2\pi v^2}{h} \int_{-\infty}^{+\infty} \rho(E) \exp \left( - \frac{(E - E_0 + \lambda)^2}{4kT} \right) \exp \left( - \frac{E_f - E}{kT} \right) dE,$$

(21)

Calculation under the assumption of $\rho(E) \approx \rho(E_f)$ yields

$$w_a = \frac{2\pi}{h} v^2 \rho(E_f) \exp \left( - \frac{\Delta E^0}{kT} \right) \exp \left( \frac{e(1 - \alpha)\eta}{kT} \right),$$

(22)

In Eq. (22), activation energy $\Delta E^0$ is defined as,

$$\Delta E^0 = -(\epsilon_0 + \Delta \epsilon_f + eV_{eq}).$$

(23)

Now we define the energy level of the electron donor near the electrode surface $E_a$ as

$$E_a = \epsilon_0 + \Delta \epsilon_f - e\eta = E_0.$$

(24)

In Eqs. (23) and (24) $\epsilon_0$ represents the energy level of the occupied energy level of the electron donor D in the absence of the interaction on the electrode surface and overpotential.

The energy term $\Delta \epsilon_f$ of Eqs. (23) and (24) represents the interaction energy of the redox species $D^+$ and $D$ on the electrode surface.4,11 The third term $-e\eta$ represents the effect of the screened overpotential on the energy level $\epsilon_0$ of the electron donor.10 Thus Eq. (24) indicates that the occupied energy level of the electron donor $D$ shifts by the interaction on the electrode surface and by the effect of the overpotential imposed on the electrode.

Equation (24) is derived by taking into consideration the interaction energy of the redox species on the electrode surface at the final and initial states of the electron transfer as well as the effect of the screened overpotential on the energy level of the electron donor.8,10

Equation (22) is also written as,

$$w_a = \frac{2\pi}{h} v^2 \rho(E_f) \exp \left( - \frac{E_f - E_a}{kT} \right).$$

(25)

From Eqs. (7) and (25)

$$k_a = \frac{2\pi e}{h} v^2 \gamma T \rho(E_f) \exp \left( - \frac{E_f - E_a}{kT} \right),$$

(26)

is obtained as the anodic reaction rate $k_a$.

When the activation energy of anodic electron transfer $\Delta E_a$ is defined as $\Delta E_a = E_f - E_a$, Eq. (26) is expressed as,

$$k_a = \frac{2\pi e}{h} v^2 \gamma T \rho(E_f) \exp \left( - \frac{\Delta E_a}{kT} \right).$$

(27)

Now let’s consider the physical meaning of Eq. (25). Figure 5a illustrates the effect of imposed overpotential $\eta$ on the anodic electrode reaction.

Electrons in the highest occupied molecular orbital of the electron donors ($E_a = E_0$) interact with holes of the metal electrode at the same energy level. The hole density of the metal electrode at the same energy level with the highest occupied molecular orbital of the electron donors ($E_a = E_0$) is

$$\rho(E) \exp \left( - \frac{\Delta E_a}{kT} \right).$$

Electron transfer takes place from the electron donors to the metal electrode by the interaction with the electron transfer energy $\nu$. Anodic electron transfer rate $k_a$ of Eq. (27) represents the electron transfer rate.11

When the imposed overpotential $\eta$ is increased, the Fermi level ($E_f = -eV$) of the electrode shifts downwards and the activation energy $\Delta E_a$ is decreased, as is shown Fig. 5a. This decreased $\Delta E_a$ increases exponentially the anodic electron transfer rate of Eqs. (26) and (27). This explains well the effect of the overpotential $\eta$ on the metal electrode. In the weak coupling case, Eq. (13) is obtained for cathodic electron transfer rate $k_c$.

The physical meaning of Eq. (13) is clear. Figure 5b illustrates the physical meaning of Eq. (13). Cathodic electron transfer takes place from metal electrode to the unoccupied molecular orbital of the electron acceptors near the electrode surface at the energy level $E_a$ of the electron acceptor by interaction with the electron transfer.
energy V. The electron density of the metal electrode at energy level $E_a$ is equal to $\rho(E_f) \exp \left( -\frac{\Delta E_a}{kT} \right)$.

The cathodic electron transfer takes place from the thermally excited electrons in the metal electrode (cathode) to the electron acceptors near the electrode surface at the equal energy level $E_a$. The cathodic electron transfer rate $k_c$ represents its rate.

When the imposed overpotential is increased into the negative direction, the Fermi level of the electrode $E_f = -eV$ shifts upward and the activation energy $\Delta E_c$ decreases. This decreased $\Delta E_c$ increases the cathodic electron transfer rate, as is seen in Eq. (13). This explains well the effect of the overpotential imposed on the metal electrode (cathode), as shown in Fig. 5b.

Now, let’s calculate the anodic current density $i_a$. Equations (8) and (22) yield

$$i_a = \frac{2\pi e}{h} \sqrt{\gamma r_d c} \rho(E_f) \exp \left( -\frac{\Delta E_a^0}{kT} \right) \exp \left( \frac{e(1 - \alpha)\eta}{kT} \right)$$

(28)

Since the exchange current density $i_{eq}^0$ is the current at $\eta = 0$, $i_a^0 = \frac{2\pi e}{h} \sqrt{\gamma r_d c} \rho(E_f) \exp \left( -\frac{\Delta E_a^0}{kT} \right)$

(29)

is obtained from Eq. (28) as the exchange current density. Equations (28) and (29) yield

$$i_a = i_a^0 \exp \left( \frac{e(1 - \alpha)\eta}{kT} \right)$$

(30)

Equation (30) is in a similar form as the classical Butler-Volmer equation which is successfully used to explain the potential dependence of the anodic current. As is shown in Eq. (29), $\Delta E_a^0$ defined in Eq. (23) is the activation energy of the exchange current density $i_{eq}^0$.

Figure 6 illustrates the physical meaning of the activation energy of the exchange current density of $i_{eq}^0$. At the electrode potential of $V$, the Fermi level of the electrode is located at $E_f = -eV$. From Eqs. (15), (23), (24) and $E_f = -eV$,

$$i_a = i_{eq}^0 \exp \left( -\frac{e(1 - \alpha)\eta}{kT} \right)$$

(31)

is obtained.

At the equilibrium potential of $\eta = 0$, Eq. (31) gives

$$\Delta E_a^0 = E_f - E_d$$

(32)

The physical meaning of the exchange current density of Eq. (29) is shown in Fig. 6. At the equilibrium potential of $\eta = 0$, Fermi level of the metal electrode is located at $E_f = -eV$. Electrons at $E_d$ in the electron donor D interact with holes of the metal electrode and flow to the metal electrode. Its magnitude is equal to the exchange current density $i_{eq}^0$ of Eq. (29). The activation energy of holes $\Delta E_a^0$ is equal to $E_f - E_d$ from Eq. (32).

2.4 Summary of anodic and cathodic processes

Current-overpotential relations are summarized from Eqs. (10) and (29), as follows.

Cathodic Current:

$$i = i_{eq} \exp -\frac{e(1 - \alpha)\eta}{kT} \eta$$

(10)

Anodic Current:

$$i_a = i_{eq}^0 \exp \left( \frac{e(1 - \alpha)\eta}{kT} \right)$$

(30)

On the other hand, current-overpotential relations in the classical electrochemistry are written, as follows.

Cathodic Current:

$$i = i_{eq} \exp -\frac{ea}{kT} \eta$$

(31)

Anodic Current:

$$i_a = i_{eq}^0 \exp \left( \frac{e(1 - \alpha)\eta}{kT} \right)$$

(32)

In Eqs. (c-1) and (c-2), $\alpha$ represents transfer coefficient. Eqs. (c-1) and (c-2), which represent current-overpotential relations in the classical electrochemistry, resemble Eqs. (10) and (30) in the quantum electrochemistry, respectively. However, its interpretation is quite different because of different interpretation of the exchange current density and transfer coefficient $\alpha$, as discussed later.

In the classical electrochemistry current-overpotential relation at any potential is expressed by the following Butler-Volmer equation.

$$i = i_{0} \left\{ \exp -\frac{ea}{kT} \eta - \exp \left( \frac{e(1 - \alpha)\eta}{kT} \right) \right\}$$

(33)

Butler-Volmer equation plays important role in the classical electrochemistry, since it describes current-overpotential relation at any potential.
An equilibrium condition of \( \eta = 0 \text{ V} \), Eqs. (10) and (30) yield
\[
i_0 = i_0 = i_0
\] (33)

Then, Eqs. (10) and (30) are unified into the following equation.
\[
i = i_0 \exp \left\{ -\frac{E(1 - \alpha)}{kT} - \frac{e(1 - \alpha)}{\eta} \right\}
\] (34)

Equation (34) is considered as quantum mechanical Butler-Volmer equation. Quantum mechanical Butler-Volmer equation of Eq. (34) resembles well Butler-Volmer equation of Eq. (c-3) in the classical electrochemistry.

Although theoretical approach and method of Quantum Electrochemistry is quite different from the Classical Electrochemistry, current-overpotential relation resembles well each other. This good resemblance (or correspondence) is advantageous point when one learns “Quantum Electrochemistry”.

### 2.5 Consideration of equilibrium condition: Quantum mechanical Nernst equation

Now let’s consider equilibrium condition in Quantum electrochemistry. Cathodic and anodic components of the exchange current density are given by Eqs. (11) and (29), respectively.

At equilibrium, Eq. (33) should hold. Then, Eqs. (11), (29) and (33) yield
\[
\frac{2\pi e}{h} v^2 \gamma r_a C_0 \rho(E_f) \exp - \frac{\Delta E_a^0}{kT} = \frac{2\pi e}{h} v^2 \gamma r_a C_0 \rho(E_f) \exp - \frac{\Delta E_a^0}{kT}
\] (35)

From Eq. (35)
\[
\frac{2\pi e}{h} v^2 \gamma r_a C_0 \rho(E_f) \exp - \frac{\Delta E_a^0}{kT} = \exp - \frac{\Delta E_a^0 - \Delta E_a^0}{kT}
\] (36)

is obtained. Now, let’s assume
\[
\frac{2\pi e}{h} v^2 \gamma r_a C_0 \rho(E_f)
\] (37)

Under the assumption of Eq. (37),
\[
\frac{C_a}{C_R} = \exp - \frac{\Delta E_a^0 - \Delta E_a^0}{kT}
\] (38)

is obtained.

Figure 7 illustrates the activation energies of \( \Delta E_a^0 \) and \( \Delta E_a^0 \). The activation energies of \( \Delta E_a^0 \) and \( \Delta E_a^0 \) are defined as,
\[
\Delta E_a^0 = E_a^0 - E_f
\] (13-1)
\[
\Delta E_a^0 = E_f - E_a^0
\] (32)

From Eqs. (13-1) and (32)
\[
\Delta E_a^0 - \Delta E_a^0 = E_f - E_a^0 - (E_f^0 - E_a^0)
\] (39)

is obtained. By taking logarithm of Eq. (38),
\[
\ln \frac{C_a}{C_R} = - \frac{\Delta E_a^0 - \Delta E_a^0}{kT}
\] (40)

is obtained. Insertion of Eq. (39) into Eq. (40) yields
\[
\ln \frac{C_a}{C_R} = \exp - \frac{2E_f - (E_a^0 + E_a^0)}{kT}
\] (41)

Equation (41) yields
\[
E_f = \frac{E_a^0 + E_a^0}{2} - \frac{kT}{2} \ln \frac{C_a}{C_R}
\] (42)
When Boltzmann distribution is also assumed for the hole concentration $p$ in electron donors (Reduced species, $C_R$),

$$p = C_R \exp \left( -\frac{E_f - E_d^0}{kT} \right)$$  \hspace{1cm} (47)

is obtained. Here electron donating level $E_d^0$ of Reduced species ($C_R$) corresponds to the valence band of semiconductor.

In Fig. 8 the right hand side corresponds to electrolyte solution and the left hand side corresponds to metal electrode. At equilibrium, $p = n$ holds. From this condition

$$C_o \exp \left( \frac{E_o^0 - E_f}{kT} \right) = C_R \exp \left( -\frac{E_f - E_d^0}{kT} \right)$$  \hspace{1cm} (48)

is obtained from Eqs. (46) and (47).

Equation (48) yields

$$C_o \exp \left( \frac{E_o^0 - E_f}{kT} \right) = C_R \exp \left( -\frac{2E_f - (E_d^0 + E_o^0)}{kT} \right)$$  \hspace{1cm} (49)

By taking logarithm of Eq. (49),

$$E_f = \frac{(E_d^0 + E_o^0)}{2} - \frac{kT}{2} \ln \frac{C_o}{C_R}$$  \hspace{1cm} (50)

is obtained. Equation (50) is equal to Eq. (42).

Equation (50) is seen in a typical textbook of semiconductor device. Thus Eq. (42) is derived easily by using a semiconductor-metal model of Fig. 8.

2.7 Summary of transition probability $W$

Transition Probability of Anodic Reaction is

$$w_a = \frac{2\pi}{\hbar} v^2 \rho(E_f) \exp \left( -\frac{\Delta E^0_a}{kT} \right) \exp \left( \frac{e(1-a)\eta}{kT} \right)$$  \hspace{1cm} (22)

Transition probability of cathodic electron transfer is given by

$$w_c = \frac{2\pi}{\hbar} v^2 \rho(E_f) \exp \left( -\frac{\Delta E^0_c}{kT} \right) \exp \left( -\frac{e(1-a)\eta}{kT} \right)$$  \hspace{1cm} (51)

Since Eq. (22) resembles Eq. (51), they are unified in the following equation.

$$w = \frac{2\pi}{\hbar} v^2 \rho(E_f) \exp \left( -\frac{\Delta E}{kT} \right) \exp \left( \pm \frac{e(1-a)\eta}{kT} \right)$$  \hspace{1cm} (52)

In Eq. (52) subscripts and superscripts a and c are omitted to obtain a simplified equation for the transition probability. In Eq. (52) $+$ sign corresponds to the anodic process and $-$ sign corresponds to the cathodic process.

2.8 Tafel equation

At large negative overpotentials, the anodic component is negligible in Eq. (34). Then,

$$i = i_0 \exp \left( -\frac{e(1-a)\eta}{kT} \right)$$  \hspace{1cm} (10)

is obtained. By taking logarithm of Eq. (10),

$$\ln i = \ln i_0 - \frac{e(1-a)\eta}{kT}$$  \hspace{1cm} (t-1)

is obtained. Equation (t-1) yields

$$\eta = \frac{kT}{e(1-a)} \ln \frac{i_0}{i} - \frac{2.3kT}{e(1-a)} \log i$$  \hspace{1cm} (t-2)

Here we define constant $a$ and $b$ as follows,

$$a = \frac{2.3kT}{e(1-a)} \log i_0, \quad b = -\frac{2.3kT}{e(1-a)}$$  \hspace{1cm} (t-3)

Then, Eq. (t-2) becomes

$$\eta = a + b \log i$$  \hspace{1cm} (t-4)

Equation (t-4) is well known as Tafel equation.

When constant $b$ is calculated for $\alpha = 0.5$ and $T = 298 K$, 0.118 V is obtained. $b = 0.118 V$ is typical Tafel slope which is well known in the classical electrochemistry. As is seen in Tafel equation, Quantum Electrochemistry corresponds well to the Classical Electrochemistry based on the transition state theory.

2.9 Quantum mechanical expression of standard rate constant and exchange current density

Standard rate constant $k^0$ is the most important kinetic parameter in classical electrochemistry. For the particular case $C_o^a = C_R^a = C$ (C$^a_o$ and C$^a_R$ are the bulk concentrations) and $V_{eq} = V_o$, the exchange current density $i_0$ can be expressed by using the standard rate constant $k^0$ as

$$i_0 = ek^0C$$  \hspace{1cm} (53)

In the quantum mechanical electron transfer theory at metal electrode, the exchange current density $i_0$ can be written from Eqs. (11) and (29) in a unified equation as,

$$i_0 = \frac{2\pi}{\hbar} v^2 \gamma r_c \rho(E_f) \exp \left( -\frac{\Delta E}{kT} \right)$$  \hspace{1cm} (54)

Because the cathodic exchange current density should be equal to the anodic one at equilibrium, subscripts and superscripts a and c are omitted from $i_0$ and $\Delta E$ in order to obtain a unified simple expression of the exchange current density, i.e., Eq. (54). Because $i_0$ of Eq. (54) should be equal to $i_0$ of Eq. (53),

$$ek^0C = \frac{2\pi}{\hbar} v^2 \gamma r_c \rho(E_f) \exp \left( -\frac{\Delta E}{kT} \right)$$  \hspace{1cm} (55)

is obtained. Equation (55) gives immediately

$$k^0 = \frac{2\pi}{\hbar} v^2 \gamma r_c \rho(E_f) \exp \left( -\frac{\Delta E}{kT} \right)$$  \hspace{1cm} (56)

Equations (54) and (56) represent the quantum mechanical expression of the standard rate constant $k^0$ and the exchange current density $i_0$, respectively. Equation (56) indicates that we can evaluate the magnitude of the electron transfer integral $v$ if the standard rate constant $k^0$, electron transfer distance $r_c$, the state density $\rho(E_f)$, temperature $T$ and the activation energy $\Delta E$ are known. Another important equation is Eq. (54). It is a quantum mechanical expression for the exchange current density. Equation (54) shows...
Current-Overpotential dependence:
\[ i = i_0 \exp \pm \frac{e(1 - \alpha)}{kT} \eta \]  

(58)

Quantum mechanical Butler Volmer Equation:
\[ i = i_0 \left( \exp - \frac{e(1 - \alpha)}{kT} \eta - \exp \frac{e(1 - \alpha)\eta}{kT} \right) \]  

(34)

Exchange current density:
\[ i_0 = \frac{2\pi e}{h} v^2 \gamma r \rho(E_f) \exp - \frac{\Delta E}{kT} \]  

(54)

Standard rate constant:
\[ k_0 = \frac{2\pi}{h} v^2 \gamma r \rho(E_f) \exp - \frac{\Delta E}{kT} \]  

(56)

Figure 9. Important Equations obtained in the Quantum electrochemistry.

that we can evaluate the magnitude of the electron transfer integral \( v \) if the data of the exchange current density \( i_0 \), the concentration of redox species \( C \), the state density of the metal electrode \( \rho(E_f) \), electron transfer distance \( \gamma r \), temperature \( T \) and the activation energy \( \Delta E \) are known.

Because equations similar to Eqs. (54) and (56) cannot be obtained in the classical electrochemistry, they are characteristic equations in the quantum electrochemistry. Equations (7), (52) and (56) yield

\[ k = w \gamma r = \frac{2\pi}{h} v^2 \gamma r \rho(E_f) \exp - \frac{\Delta E}{kT} \exp \pm \frac{e(1 - \alpha)}{kT} \eta \]  

(57)

Equations (10) and (30) yield
\[ i = i_0 \exp \pm \frac{e(1 - \alpha)}{kT} \eta \]  

(58)

In Eqs. (57) and (58), + sign corresponds to the anodic process and − sign corresponds to the cathodic process. Equations (57) and (58) show that electron transfer rate \( k \) of the electrode kinetics and the electric current depend exponentially on the imposed overpotential \( \eta \). Equation (58) corresponds well to the classical electrochemistry based on the Transition state theory.

Because in most chemical systems observed current changes exponentially depending on overpotential \( \eta \), Eq. (58) explains well the experimental results. Figure 9 summarizes important equations obtained in the quantum electrochemistry.

3. New Interpretation of Transfer Coefficient

In the classical electrochemistry based on the transition state theory, cathodic current is expressed as,
\[ i_e = i_0 \exp - \frac{e\alpha}{kT} \eta \]  

(c-1)

Where \( i_0 \) represents the exchange current density and \( \alpha_e \) transfer coefficient, respectively. Equation (c-1) is in a similar form as the corresponding quantum mechanical equation of Eq. (10). A Comparison of Eq. (c-1) with Eq. (10) gives
\[ \alpha_e = 1 - \alpha \]  

(59)

In the classical electrochemistry, transfer coefficient \( \alpha_e \) is considered to indicate the symmetry of the potential barrier of the transition state of electron transfer at the electrode.

On the other hand, in the quantum electrochemistry, parameter \( \alpha \) represents the electrostatic screening of the electrode potential by ions in the electrolyte solution between the metal electrode and redox species. Therefore it has a quite different physical meaning compared with transfer coefficient in the classical electrochemistry. Electrostatic screening of the electrode potential by ions in the electrolyte solution between the metal electrode and redox species can be discussed as follows.

In order to consider this problem, we assume that the electrolyte-electrode interface is composed of metal electrode-electric double layer-electrolyte. Electrostatic screening of the electrode potential occurs at the electric double layer and the electrolyte outside the electrode. The electrode potential imposed on the electrode is screened by ions in the electrolyte layer between the electrode and electron acceptor. This situation resembles the electrostatic screening by free electrons in metal, i.e. Thomas Fermi screening effect in solid state physics.

In the model of electrolyte-electrode interface, the electrostatic screening of the electrode potential is expressed by the product of electrostatic screening factor by the electric double layer \( \alpha_D \) and the electrostatic screening factor by the electrolyte outside of it \( \alpha_{EL} \), as follows.
\[ \alpha = \alpha_D \cdot \alpha_{EL} \]  

(60)

The electrostatic screening by the electrolyte has been studied well in the Debye-Hückel theory for electrolyte solutions. The Coulombic potential \( \Psi(r_0) \) by ion in electrolyte with charge Ze is expressed as
\[ \Psi(r_0) = \frac{Ze}{\varepsilon r_0} \exp - \chi r_0 \]  

(61)

Here \( r_0 \) represents the distance from the central ion, \( \chi^{-1} \) Debye Length, \( \varepsilon \) the dielectric constant of the electrolyte solution, respectively.

Equation (61) indicates that the Coulombic potential of the central ion is screened in the electrolyte solution. From Eq. (61) \( \alpha_{EL} \) can be given by the following equation.
\[ \alpha_{EL} = \exp - \chi r_0 \]  

(62)

From Eqs. (60) and (62)
\[ \alpha = \alpha_D \cdot \exp - \chi r_0 \]  

(63)

is obtained. According to the Debye-Hückel theory, the Debye length is expressed at room temperature \((25^\circ C)\) as
\[ \chi^{-1} = \frac{3.04 \times 10^{-8}}{\sqrt{I}} \text{ cm} \]  

(64)

Here I represent the ionic strength of the electrolyte solution. Equations (63) and (64) yields
\[ \alpha = \alpha_D \exp - \frac{r_0}{3.04 \sqrt{I}} \]  

(65)

In Eq. (65) the unit of \( r_0 \) is in Angstroms. Taking logarithm of Eq. (65), we obtain a useful equation for \( \alpha \).
\[ \ln \alpha = \ln \alpha_D - \frac{r_0}{3.04 \sqrt{I}} \]  

(66)

If this new idea of electrostatic screening for \( \alpha \) is correct, \( \ln \alpha \) should be proportional to \( \sqrt{I} \) with a negative slope of
amounts of NaCl and KCl to HCl aqueous solution. This result supports our model for the screening factor \( \alpha \) of the potential barrier of the transition state. As is seen in Eq. (66), parameter \( \alpha \) is considered as a parameter of the symmetry of the potential barrier of the transition state is considered to represent electron transfer distance \( D \), represents the thickness of the compact layer on the electrode surface. It should be noted that the information about the electron transfer distance \( r_0 \) is contained in the screening factor \( \alpha \) as well as the electrostatic screening.

### 3.1 Transfer coefficient of Fe\(^{3+}\)/Fe\(^{2+}\) redox system transfer coefficient of cathodic reaction of Fe\(^{3+}\):

Cathodic reaction of Fe\(^{3+}\) is expressed as

\[
\text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+}
\]  

(N-1)

We have determined the potential screening factor \( \alpha \) from the slope of Tafel Plot as in the case of hydrogen evolution. In the redox reaction Fe(NH\(_4\))\(_2\)(SO\(_4\))\(_2\)

\( \cdot 6\text{H}_2\text{O} \) was used as Fe\(^{3+}\) compound and Fe(NH\(_4\))\(_2\)(SO\(_4\))\(_2\)

\( \cdot 12\text{H}_2\text{O} \) was used as Fe\(^{2+}\) compound. Figure 12 shows \( \ln \alpha \) vs. \( \sqrt{I} \) plot for the cathodic reaction of Fe\(^{3+}\). As is seen in Eq. (66), \( \ln \alpha \) is proportional to \( \sqrt{I} \) and the slope is negative, as is expected theoretically from Eq. (66). The result of Fig. 12 is explained well by Eq. (66). As is seen in Fig. 12, \( \ln \alpha \) is proportional to \( \sqrt{I} \), even when the magnitude of ionic strength \( I \) is changed by adding various amounts of KCl and NaCl, which have nothing to do with the reaction, to HCl aqueous solution.

As was shown in Fig. 11, \( \ln \alpha \) is proportional to \( \sqrt{I} \), when the magnitude of ionic strength \( I \) is controlled by adding various amounts of NaCl and KCl to HCl aqueous solution. This result supports our model for the screening factor \( \alpha \).

These results are quite important. The present electrochemical theory is based on the transition state theory. The transition state of the hydrolysis of hydrogen evolution is considered to be based on the interaction between the metal electrode surface and H\(^+\) (electron acceptor). Transfer coefficient \( \alpha \) is considered as a parameter of the symmetry of the potential barrier of the transition state.\(^8,10\) The shape and symmetry of the potential barrier of the transition state is considered not to change depending on the ionic strength. However, transfer coefficient changes depending on the ionic strength \( I \), as is shown Figs. 10 and 11.

These experimental results cannot be explained by the present electrochemical theory based on the transition state theory.\(^8\) The results of Figs. 10 and 11 are able to be explained by the theory of the potential screening of Eq. (66). Table 1 shows values of \( \alpha_\text{et} \), experimental \( \alpha_c \), and theoretical \( \alpha_c \) evaluated by analyzing the \( \ln \alpha \) dependence of \( \alpha \) for hydrogen evolution at Pt electrode in various acidic solutions.\(^9,10\) As is seen in Table 1, theoretical \( \alpha_c \) calculated by Eq. (66) agrees quantitatively with experimental \( \alpha_c \).

#### Table 1. Ionic strength (I) dependence of transfer coefficients for hydrogen evolution at Pt electrode in various electrolyte solutions together with the values of \( \alpha_\text{et} \) and \( r_0 \).

| Electrolyte Solutions | Ionic Strength I | \( \alpha_c \) (Exp.) | \( \alpha_c \) (Calc.) | \( \delta_0 \) \( r_0/\text{Å} \) |
|-----------------------|-----------------|----------------------|----------------------|----------------------|
| HCl                   | 0.5             | 0.18                 | 0.18                 |                      |
|                       | 0.25            | 0.17                 | 0.17                 |                      |
|                       | 0.1             | 0.16                 | 0.16                 |                      |
|                       | 0.05            | 0.16                 | 0.16                 |                      |
|                       | 0.01            | 0.16                 | 0.05                 |                      |
|                       | 0.001           | 0.15                 | 0.15                 |                      |
| 0.005M HCl + NaCl     | 0.5             | 0.27                 | 0.26                 |                      |
| (varied)              | 0.105           | 0.19                 | 0.21                 |                      |
|                       | 0.055           | 0.18                 | 0.20                 | 0.837 0.535          |
|                       | 0.015           | 0.20                 | 0.18                 |                      |
|                       | 0.01            | 0.19                 | 0.18                 |                      |

Now let's consider the physical meaning of parameter \( r_0 \) which appears in Eqs. (65) and (66). Table 1 gives values of \( r_0 \) determined by Eq. (66). As is seen in Eq. (61), parameter \( r_0 \) represents the distance from the potential source to the place where potential is imposed. In the present model electrostatic screening expressed by Eq. (61) represents the screening by ions in an electrolyte solution that extends outside the electric double layer.

In the electrochemical electron transfer, parameter \( r_0 \) is considered to represent electron transfer distance \( r_\text{et} \) that is defined as

\[
r_\text{et} = \delta_0 + r_0
\]  

(67)

Where \( \delta_0 \) represents the thickness of the compact layer on the electrode surface. It should be noted that the information about the electron transfer distance \( r_0 \) is contained in the screening factor \( \alpha \) as well as the electrostatic screening.

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**Figure 10.** \( \ln \alpha \) vs. \( \sqrt{I} \) plot for hydrogen evolution at Pt electrode from HCl aqueous solutions.

**Figure 11.** \( \ln \alpha \) vs. \( \sqrt{I} \) plot for hydrogen evolution at Pt electrode from 0.05 M HCl aqueous solutions. Ionic strength \( I \) of the electrolyte was changed by adding various amount of NaCl.

**Figure 12.** \( \ln \alpha \) vs. \( \sqrt{I} \) plot for the cathodic reaction of Fe\(^{3+}\), i.e. (N-1).
that our potential screening theory for transfer coefficient can be applied to the cathodic reaction of Fe$^{3+}$ Eq. (N-1).

In $\alpha_0 = -0.119$ and $r_0 = 0.173$ Å were obtained from the intercept with y axis of a ln $\alpha$ vs. $\sqrt{I}$ plot and the slope, respectively, by the same way as in the case of hydrogen evolution.\(^{10}\)

The experimental equation that represents ln $\alpha$ vs. $\sqrt{I}$ plot in Fig. 12 is

$$\ln \alpha = -0.119 - 0.0571 \sqrt{I} \quad \text{(N-2)}$$

Screening factor $\alpha$ at I can be calculated by inserting the value of each ionic strength I into Eq. (N-2). Once the screening factor $\alpha$ is obtained, the value of Transfer coefficient $\alpha_i$ can be obtained from the screening factor $\alpha$ by using the relation $\alpha_i = 1 - \alpha$.

Table 2 shows experimental value of transfer coefficient $\alpha_i$ (exp) for the cathodic reaction Eq. (N-1) and the transfer coefficient $\alpha_i$ (calc) calculated from Eq. (N-2). As is seen in Table 2, experimental value of transfer coefficient $\alpha_i$ (exp) agrees well with the value of the calculated transfer coefficient $\alpha_i$ (calc). This result supports our potential screening theory for transfer coefficient.\(^{27}\)

3.2 Transfer coefficient of anodic reaction of Fe$^{2+}$

Anodic reaction of Fe$^{2+}$ is expressed as,

$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e \quad \text{(N-3)}$$

In the case of anodic reaction of Fe$^{2+}$ Eq. (N-3), the potential screening factor $\alpha$ can be obtained from the $Tafel$ slope by using Eq. (30) similarly as in the case of cathodic reaction.

Figure 13 shows ln $\alpha$ vs. $\sqrt{I}$ plot for the anodic reaction of Fe$^{2+}$ Eq. (N-3).\(^{27}\) As is seen in Fig. 13, ln $\alpha$ is proportional to $\sqrt{I}$ and the slope is negative, as is expected theoretically from Eq. (66). The result of Fig. 13 is explained well by Eq. (66). This result shows that our potential screening theory for transfer coefficient can be applied to the anodic reaction of Fe$^{2+}$, i.e. Eq. (N-1).

In $\alpha_0 = -0.168$ and $r_0 = 0.091$ Å were obtained from the intercept with y axis of a ln $\alpha$ vs. $\sqrt{I}$ plot and the slope, respectively, by the same way as in the case of hydrogen evolution.\(^{10,27}\)

### Table 2. Experimental and calculated value of transfer coefficient $\alpha_i$ (exp) and $\alpha_i$ (calc) for the cathodic reaction Eq. (N-1).

| I   | $\alpha_i$ (exp) | $\alpha_i$ (calc) |
|-----|------------------|------------------|
| 0.910 | 0.16             | 0.16             |
| 0.840 | 0.17             | 0.16             |
| 0.699 | 0.15             | 0.15             |
| 0.560 | 0.15             | 0.15             |
| 0.280 | 0.14             | 0.14             |
| 0.140 | 0.13             | 0.13             |

![Figure 13](image_url)  
**Figure 13.** ln $\alpha$ vs. $\sqrt{I}$ plot for the anodic reaction of Eq. (N-3).

The experimental equation that represents ln $\alpha$ vs. $\sqrt{I}$ plot in Fig. 13 is

$$\ln \alpha = -0.168 - 0.0301 \sqrt{I} \quad \text{(N-4)}$$

Screening factor $\alpha$ at each I can be calculated by inserting the I value into Eq. (N-4). Once the screening factor $\alpha$ is obtained from Eq. (N-4), the value of Transfer coefficient $\alpha_i$ can be obtained from the screening factor $\alpha$ by using the relation $\alpha_i = 1 - \alpha$. Table 3 shows experimental value of transfer coefficient $\alpha_i$ (exp) together with the calculated transfer coefficient $\alpha_i$ (calc) that was calculated from Eq. (N-4).

As is seen in Table 3, experimental value of transfer coefficient $\alpha_i$ (exp) agrees well with the value of the calculated transfer coefficient $\alpha_i$ (calc) for the anodic reaction of Eq. (N-3) and the transfer coefficient $\alpha_i$ (calc) calculated from Eq. (N-4). This result indicates that our potential screening theory for transfer coefficient is a general theory that can be also applied to anodic reactions.

### Table 3. Experimental value of transfer coefficient $\alpha_i$ (exp) for the anodic reaction of Eq. (N-3) and the transfer coefficient $\alpha_i$ (calc) calculated from Eq. (N-4).

| I   | $\alpha_i$ (exp) | $\alpha_i$ (calc) |
|-----|------------------|------------------|
| 0.910 | 0.19             | 0.18             |
| 0.840 | 0.17             | 0.18             |
| 0.700 | 0.17             | 0.18             |
| 0.560 | 0.17             | 0.17             |
| 0.280 | 0.16             | 0.17             |
| 0.140 | 0.16             | 0.16             |
| 0.070 | 0.16             | 0.16             |
| 0.035 | 0.17             | 0.16             |
| 0.014 | 0.16             | 0.16             |

3.3 Is the theory of transfer coefficient of the classical electrochemistry correct?

In the classical electrochemistry current-overpotential relation at any potential is expressed by the following Butler-Volmer equation.\(^{9}\)

$$i = i_e + i_b \left[ \exp \left( \frac{1 - \alpha_i} {kT} \eta \right) - \exp \left( -\frac{\alpha_i} {kT} \eta \right) \right] \quad \text{(c-3)}$$

In Eq. (c-3) $i_b$ represents the exchange current and $\alpha_i$ transfer coefficient, respectively. Now, let’s write transfer coefficient of anodic reaction as $\alpha_i^+$ and transfer coefficient of cathodic reaction as $\alpha_i^-$. Then Eq. (c-3) yields

$$\alpha_i^+ + \alpha_i^- = (1 - \alpha_i) + \alpha_i = 1.0 \quad \text{(N-5)}$$

Table 4 shows transfer coefficient $\alpha_i$ of the cathodic reaction of Eq. (N-1) and the transfer coefficient $\alpha_i^+$ of the anodic reaction of Eq. (N-3) and their sum $\alpha_i^+ + \alpha_i^-$ (exp). As is shown in this table, the value of $\alpha_i^+ + \alpha_i^-$ (exp) is in the range of 0.29–0.35 at any ionic strength.

Since these value is far from 1.0 expected from Eq. (N-5), we can conclude that Eq. (N-5) does not hold. This result makes us doubt the theory of transfer coefficient of the classical electrochemistry based on the transition state theory.\(^{27}\)

On the other hand, our potential screening theory yields the following equation from Eqs. (10) and (30).

$$\alpha_i^+ + \alpha_i^- = (1 - \alpha) + (1 - \alpha) = 2 - 2\alpha \quad \text{(N-6)}$$

Where $\alpha_i$ represents parameter which corresponds to transfer coefficient of anodic reaction and $\alpha_i$ parameter which corresponds to transfer coefficient of cathodic reaction in the quantum electro-
4. Application to Hydrogen Evolution Reaction

4.1 Mechanism of hydrogen evolution

As for the rate determining step of hydrogen evolution reaction, the following two mechanisms are considered.19

1) Electron Transfer of Eq. (H-1) is the rate determining step.

\[ \text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ad}} \]  \hspace{1cm} (H-1)

Where \(\text{H}_{\text{ad}}\) represents an atomic hydrogen adsorbed on the electrode surface.

2) Recombination reaction of Eq. (H-2) (Tafel Reaction) is the rate determining step.

\[ \text{H}_{\text{ad}} + \text{H}_{\text{ad}} \rightarrow \text{H}_2 \]  \hspace{1cm} (H-2)

3) Besides Eqs. (H-1) and (H-2) an electrochemical mechanism is proposed, where following reaction is the rate determining step.

\[ \text{H}_2^+ + \text{e}^- \rightarrow \text{H}_2 \]  \hspace{1cm} (H-3)

4.2 Problem of hydrogen evolution reaction

Hydrogen evolution is one of the most fundamental electrochemical reactions. A large number of electrochemists have studied this reaction. One of the most mysterious problems of this reaction is that the reaction rate depends remarkably on the kind of electrode material and the magnitude of the exchange current density at Pt electrode is 10^4 times larger than at Hg electrode.21 What is the role of metal electrode?

Why the electrode reaction rate differs depending on the kind of the electrode material? Classical electrochemistry does not answer this problem. Quantum electrochemistry can answer this problem as follows.

The exchange current density and the activation energy \(\Delta E^0_{\text{c}}\) of cathodic reaction are expressed from Eqs. (11) and (12), as follows,

\[ i_0 = \frac{2\pi e \text{v}^2}{h} \gamma_{r_0} C_0 \rho(E_f) \exp \left( \frac{-\Delta E^0_{\text{c}}}{kT} \right) \]  \hspace{1cm} (11)

\[ \Delta E^0_{\text{c}} = \varepsilon_0 - \Delta \varepsilon_{\text{e}} + eV_{\text{eq}} \]  \hspace{1cm} (12)

At equilibrium (\(\eta = 0\) V), Fermi level of the electrode is located at \(E_f = -eV_{\text{eq}}\). Energy level of electron acceptor is located at \(\varepsilon_0\). Electrons at electrode surface interact with electron acceptors with the transfer energy \(\varepsilon_0\). Electron density of thermally excited electrons at the electrode surface is \(\rho(E_f) \exp \left( \frac{-\Delta E^0_{\text{c}}}{kT} \right)\). Electron transfer of those thermally excited electrons takes place from the electrode surface to \(E = \varepsilon_0\) of electron acceptor near the electrode surface.

The exchange current density is the current accompanied with the electron transfer. Figure 14 illustrates physical meaning of the exchange current density of Eq. (11). As is shown in Eq. (11), the magnitude of the exchange current density \(i_0\) changes sensitively depending on the activation energy \(\Delta E^0_{\text{c}}\).

Equation (12) shows that the activation energy is determined by the energy level of electron acceptor, Fermi level of the electrode \(E_f = -eV_{\text{eq}}\) and “electron transfer adsorption energy” \(\Delta \varepsilon_{\text{e}}\).

For hydrogen evolution, energy level of the electron acceptor (proton) is fixed. Fermi level of the electrode is set at a constant value \(E_f = -eV_{\text{eq}}\). The magnitude of electron transfer adsorption energy \(\Delta \varepsilon_{\text{e}}\) changes depending on the kind of electrode material.

\[ \Delta \varepsilon_{\text{e}} = \varepsilon_{\text{act}, f} - \varepsilon_{\text{act}, j} \]  \hspace{1cm} (68)

In the Eq. (68), \(\varepsilon_{\text{act}, f}\) represents the adsorption energy of the atomic hydrogen \(H\) on the electrode surface at the final state of the electron transfer which is formed at the same instant with the cathodic electron transfer of Eq. (H-1).
\[ \varepsilon_{\text{int}} \approx \varepsilon_{\text{int},f} = \beta E_{M-H} \]  

(69)

is considered to hold. Under this condition,

\[ \Delta \varepsilon_{\text{int}} = \varepsilon_{\text{int}} - \varepsilon_{\text{int},f} \]  

(70)

can be assumed. Here \( E_{M-H} \) represents the adsorption energy of atomic hydrogen on a metal surface in the vacuum. Parameter \( \beta \) represents the shielding factor by which the adsorption energy of hydrogen is shielded by a solvent layer near the electrode.

Equations (10), (11), (12) and (70) yield the exchange current density of hydrogen evolution \( i_{0,H} \).

\[ \begin{align*}
\log i_{0,H} &= \frac{2\pi e}{h} v r_i C(E_f) \exp \left( -\frac{e_0 - \beta E_{M-H} + eV_{eq}}{kT} \right) \\
&= \log C^* \frac{\beta E_{M-H}}{2.303kT}
\end{align*} \]  

(71)

(72)

(73)

Taking logarithm of Eq. (73), we obtain

\[ \log i_{0,H} = \log C^* + \frac{\beta E_{M-H}}{2.303kT} \]  

(74)

Equation (74) indicates that \( \log i_{0,H} \) plotted against \( E_{M-H} \) should be on a straight line if the present theory is correct. Figure 16 shows \( \log i_{0,H} \) plotted against \( E_{M-H} \) on various kind of metal electrodes.

\[ \beta \approx 0.40 \]  

(75)

is obtained. By solving Eq. (75), \( \beta = 0.40 \) is obtained.

From the above discussion, we can conclude that the left hand branch of Fig. 16 \( (E_{M-H} < 2.6 \text{ eV}) \) is the electron transfer limited region. The left hand branch of Fig. 16 \( (E_{M-H} < 2.6 \text{ eV}) \) can be explained well by Eq. (74) with \( \beta = 0.40 \). Equation (74) was derived by using assumption of Eqs. (69) and (70). It means that “cathodic electron transfer adsorption” of atomic hydrogen at the final state of electron transfer plays important role in the hydrogen evolution, as was illustrated in Fig. 15.

In Fig. 16 \( \log i_{0,H} \) in the right hand branch \( (E_{M-H} > 2.6 \text{ eV}) \) decreases with increasing \( E_{M-H} \). How is this right hand branch \( (E_{M-H} > 2.6 \text{ eV}) \) explained? This region is also related with the mechanism of hydrogen evolution, as follows. \( E_{M-H} > 2.6 \text{ eV} \) the movement of atomic hydrogen adsorbed on the electrode surface is thought to become more difficult with increased adsorption energy. Then the rate determining step of hydrogen evolution is thought to be recombination of atomic hydrogen of Eq. (H-2).

4.3 Rate determining step: Recombination

When reaction rate \( k \) of recombination (Eq. (H-2)) is the rate determining step, the reaction rate \( k \) would be expressed as,

\[ k \approx \exp \left( -\frac{\Delta G_{\text{rec}}}{kT} \right) \]  

(76)

Where \( \Delta G_{\text{rec}} \) represents the free energy of activation for the reaction (Eq. (H-2)). Figure 17 shows potential energy of Recombination reaction of Eq. (H-2).

As is shown in Fig. 17, \( \Delta G_{\text{rec}} \) is expressed approximately as,

\[ \Delta G_{\text{rec}} = \Delta \varepsilon_{\text{ad}} - \frac{1}{2} D(H-H) \]  

(77)

Where \( D(H-H) \) is the bonding energy of \( H_2 \) and \( \Delta \varepsilon_{\text{ad}} \) is the adsorption energy of atomic hydrogen on the electrode surface. Since \( D(H-H) = 4.48 \text{ eV} \), we obtain

\[ \Delta G_{\text{rec}} = \Delta \varepsilon_{\text{ad}} - 2.24 \]  

(78)

Figure 17. Potential energy diagram of Free Energy of Activation for the Recombination reaction of Eq. (H-2).
Equations (76) and (78) yield
\[ k \approx \exp \left( -\frac{\Delta E_{ad} - 2.24}{kT} \right) \]  
(79)

By taking logarithm of Eq. (79), we obtain we obtain
\[ \log k = \frac{\Delta E_{ad} - 2.24}{2.3kT} + \frac{2.24}{2.3kT} \]  
(80)

Here, let’s assume Eq. (70) for \( \Delta E_{ad} \). Under this assumption, Eq. (80) yields
\[ \log k = C - \frac{\beta E_{M-H}}{2.3kT} \]  
(81)

Where \( C = \frac{2.24}{2.3kT} \) is considered as a constant.

Since the exchange current density is proportional to reaction rate, as is seen in Eq. (53), we can assume \( \log i_{0,H} = \log k \). Under this assumption, Eq. (81) yields
\[ \log i_{0,H} = C - \frac{\beta E_{M-H}}{2.3kT} \]  
(82)

Equation (82) shows that \( \log i_{0,H} \) is proportional to \( E_{M-H} \) with a negative slope.

Actually \( \log i_{0,H} \) decreases proportionally to \( E_{M-H} \) (with a negative slope) in the right hand side of Fig. 16, i.e. in the region of \( E_{M-H} \approx 2.6 \text{ eV} \). The slope is 6.65 eV⁻¹. Therefore we obtain from Eq. (82)
\[ -\frac{\beta}{2.3kT} = -6.65 \text{ eV}^{-1} \]  
(83)

By calculating Eq. (83), \( \beta \approx 0.39 \) is obtained.

Thus, the right hand side of Fig. 16 can be explained by the above recombination theory. Moreover \( \beta \approx 0.39 \) is very close to \( \beta = 0.40 \) that was obtained from the left branch of Fig. 16 (\( E_{M-H} \approx 2.6 \text{ eV} \)).

As was shown in the above discussion, Volcano shaped dependence of \( \log i_{0,H} \) on \( E_{M-H} \) of Fig. 16 is well explained by our theory of Quantum Electrochemistry. It should be noted that the classical electrochemical theory based on the transition state theory cannot explain the Volcano shaped dependence of \( \log i_{0,H} \) on \( E_{M-H} \) of Fig. 16.

Since quantum electrochemistry can take into consideration the interaction of redox species on the electrode surface, as in Eq. (70), this kind of explanation has become possible for the first time.\(^4\)

### 4.4 Quantitative calculation of exchange current density \( i_{0,H} \)

Quantum electrochemistry can calculate the magnitude of the exchange current density \( i_{0,H} \) for hydrogen evolution by using Eq. (70).\(^9\)

Now let’s define \( \Delta E \) and \( I_0 \) by the following equations.
\[ \Delta E = \varepsilon_0 - \Delta \varepsilon_p + e V_{eq} \]  
(84)
\[ I_0 = \frac{2\pi e}{\hbar} \gamma^2 C_A \rho(E_f) \]  
(85)

In Eq. (85) \( C_A = \gamma \rho_0 C \).

Then, the exchange current density of hydrogen evolution \( i_{0,H} \) of Eq. (71) can be expressed by the following simple equation.
\[ i_{0,H} = I_0 \exp \left( -\frac{\Delta E}{kT} \right) \]  
(86)

As is seen in Eq. (86), \( \Delta E \) defined in Eq. (84) is equal to the activation energy of the exchange current density of hydrogen evolution \( i_{0,H} \). For the “electron transfer adsorption energy” \( \Delta \varepsilon \), we assume the same relation as in Eq. (70). Then Eq. (84) yields
\[ \Delta E = \varepsilon_0 - \beta E_{M-H} + e V_{eq} \]  
(87)

Equation (87) shows that \( \Delta E \) is proportional to adsorption energy of hydrogen \( E_{M-H} \) (with proportion constant = \(-\beta\)).

When \( \Delta E \) values for various metal electrodes were plotted against \( E_{M-H} \), it was found that \( \Delta E \) is almost proportional to \( E_{M-H} \). The slope of \( \Delta E \) vs. \( E_{M-H} \) plot was \(-0.40 \). This result is explained well by Eq. (87) with \( \beta = -0.40 \). Using \( \beta = -0.40 \) in Eq. (87), we obtain
\[ \Delta E = \varepsilon_0 + e V_{eq} - 0.4 E_{M-H} \]  
(88)

Since the intercept in the \( \Delta E \) vs. \( E_{M-H} \) plot at \( E_{M-H} = 0.0 \text{ eV} \) is 1.3 eV, we can assume \( \varepsilon_0 + e V_{eq} = 1.3 \text{ eV} \). Under this assumption, Eq. (88) gives
\[ \Delta E = 1.3 - 0.4 E_{M-H} \]  
(89)

Equation (89) shows that \( \Delta E \) can be obtained once \( E_{M-H} \) is known.\(^8\)

Adsorption energy of hydrogen \( E_{M-H} \) on various metals are already reported.\(^22\) By using \( E_{M-H} \) values on various metals, we can calculate \( \Delta E \) from Eq. (89). Equation (86) gives
\[ I_0 = i_{0,H} \exp \left( -\frac{\beta E_{M-H}}{kT} \right) \]  
(90)

This equation shows that \( I_0 \) can be calculated from the experimental exchange current density \( i_{0,H} \) and \( \Delta E \) from Eq. (90).

Equation (85) gives
\[ \nu^2 = \frac{\hbar \gamma^2}{2\pi e C_A \rho(E_f)} \]  
(91)

Equation (91) shows that electron transfer energy \( \nu \) for hydrogen evolution can be calculated from the values \( I_0, C_A (= \gamma \rho_0 C) \) and \( \rho(E_f) \).

The proton concentration in the experiments to measure the exchange current density for hydrogen evolution is mostly 0.1–1.0 mol dm⁻³. Let’s assume \( C_A = 3.0 \times 10^{23} \text{ dm}^{-3} \) that corresponds to a proton concentration of 0.3 mol dm⁻³. The state density \( \rho(E_f) \) for various metals was already calculated in the previous manuscript.\(^4\)

By using \( \rho(E_f) \) values in the previous manuscript\(^4\) and \( C_A = 3.0 \times 10^{23} \text{ dm}^{-3} \), we can calculate electron transfer energy \( \nu \) for hydrogen evolution from Eqs. (90) and (91) and \( I_0 \) at 8 kinds of metal electrode.\(^5\) Table 6 shows the result of electron transfer energy \( \nu \) and \( I_0 \) calculated by this method together with \( \rho(E_f) \). As already discussed, the rate determining step of hydrogen revolution reaction at 8 kinds of metal electrode in Table 6 is electron transfer reaction from Eq. (H-1). Therefore the electron transfer energy \( \nu \) expresses the magnitude of the electron transfer integral \( \nu \) for the electron transfer reaction of Eq. (H-1) at these metal electrodes.

It is noted that the magnitude of the electron transfer integral \( \nu \) for the electron transfer reaction of Eq. (H-1) is quite small, as is seen in Table 6. By substituting \( \Delta E \) and \( I_0 \) into Eq. (86), the exchange current density of hydrogen evolution \( i_{0,H} \) is calculated.\(^9\)

Table 7 shows \( E_{M-H}, I_0, \) calculated log \( i_{0,H} \) (Theory) together with experimental log \( i_{0,H} \) (Exp.).\(^9\) As is shown in Table 7, the agreement

| Metal | \( I_0 / \text{A cm}^{-2} \) | \( \rho(E_f) / 10^{16} \text{ J}^{-1} \text{ molecule}^{-1} \) | \( \nu / 10^{-8} \text{ eV} \) |
|-------|-----------------|-----------------|-----------------|
| Cu    | 1.84            | 1.86            | 3.67            |
| Ni    | 114.35          | 18.7            | 9.14            |
| Pt    | 128.05          | 18.2            | 9.78            |
| Ga    | 3439.0          | 1.59            | 172             |
| In    | 0.705           | 4.51            | 1.46            |
| Hg    | 6.37            | 4.78            | 4.26            |
| Re    | 23.34           | 6.14            | 7.2             |
| Pd    | 6896.5          | 25.2            | 61              |
between theoretically evaluated $\log_{10} \text{H}^+$ (Theory) and experimental $\log_{10} \text{H}^+$ (Exp.) is bad for Ti, Cr, Nb, Mo and W. However, it is unbelievably good for, Fe, Co, Ni, Cu, Zn, Ag, Cd, In, Sn, Au, Hg, Ti, and Pb, as is seen in Table 7.

Figure 18 shows calculated $\log_{10} \text{H}^+$ (Theory, ●) and experimental hydrogen exchange current density $\log_{10} \text{H}^+$ (Experimental, ○) plotted against $E_{M-H}$. However, the agreement between theory and experiment for Mn, Rh, Pd, Re, Pt is not very good. $E_{M-H}$ for these metal electrodes is close to 2.6 eV and is located at the transition region between weak $E_{M-H}$ ($< 2.6 \text{eV}$) and strong $E_{M-H}$ ($> 2.6 \text{eV}$) region. This suggests that the rate determining step on these metal electrodes is not pure electron transfer, but is affected by recombination due to adsorption of hydrogen. All the above results support the present theory and indicate the important role of “electron transfer adsorption” at the final state of electron transfer.

It is clear that these quantitative calculations became possible for the first time by quantum electrochemistry. However, this kind of quantitative calculation is impossible by the electrochemical theory based on the transition state theory, because the classical electrochemistry is phenomenological theory based on the Transition state theory. This means that quantum electrochemistry is more advanced than the electrochemical theory based on the transition state theory. From the above results we can classify the electrocatalytic activity of metal electrodes into three group from the view point of the mechanism of hydrogen evolution. Table 8 shows classification of metal electrodes according to the electrocatalytic activity of hydrogen evolution.

### 4.5 Theoretical evaluation of hydrogen overvoltage

Hydrogen over-voltage has been investigated from a long time ago by a large number of electrochemists. From Eq. (10) for cathodic current–overvoltage relation can be written as follows.

$$ i = i_{0,H} \exp \left\{ \frac{\epsilon(1-\alpha)}{kT} \eta_H \right\} \quad (92) $$

Where $\eta_H$ represents hydrogen over-voltage. From Eq. (92) hydrogen over-voltage $\eta_H$ can be expressed as

$$ \eta_H = \frac{2.3RT}{\epsilon(1-\alpha)} \log \left( \frac{i_{0,H}}{i} \right) \quad (93) $$

When $i = 10^{-3} \text{A cm}^{-2}$, $T = 300 \text{K}$ and $\alpha = 0.5$ is assumed in Eq. (93), Eq. (93) gives

$$ \eta_H = 0.11891 \log i_{0,H} + 3.0 \quad (94) $$

By using Eq. (94) and calculated $\log_{10} \text{H}^+$ (Theory) in Table 7 for various metal electrodes, we calculated $\eta_H$ for various metal electrodes. Table 9 shows the result. In the same table experimental values of $\eta_H$ (at $i = 10^{-3} \text{A cm}^{-2}$) in Ref. 23 are given for comparison. As is seen in Table 9, agreement between theory and experiment is satisfactory. This result supports our present theory.
5. Evaluation of Electron Transfer Integral

Exchange current density and standard rate constant are fundamental kinetic parameters of Electrochemistry. Their data has been accumulated in the past literature and books. The present theory enables us to evaluate the magnitude of the electron transfer integral \( i_0 \) from standard rate constant \( k^0 \) and the exchange current density \( i_0 \). There are the following two methods to evaluate the magnitude of the electron transfer integral \( v \).

5.1 \( k^0 \) method

The magnitude of the electron transfer integral \( v \) can be obtained by substituting values of \( k^0 \), \( \gamma r_{et} \), the state density of the metal electrode \( \rho(E_f) \), temperature \( T \), and activation energy \( \Delta E \) into Eq. (56). Let’s call this \( k^0 \) method.

5.2 \( i_0 \) method

The magnitude of the electron transfer integral \( v \) is evaluated by substituting the values of exchange current density \( i_0 \), \( \gamma r_{et} \), Temperature \( T \), activation energy \( \Delta E \) and the concentration \( C \) of the redox species into Eq. (54). Let’s call this \( i_0 \) method.

For the evaluation of the electron transfer integral \( v \) the experimental data of \( k^0 \), \( i_0 \) and \( \Delta E \) are substituted into Eq. (56) and Eq. (54), respectively. In order to evaluate the electron transfer integral \( v \), the magnitude of \( r_{et} \) is indispensable. The data of electron transfer distance \( r_{et} \) are quite few. Recently, the electron transfer distance was evaluated from ionic strength dependence of transfer coefficient for proton reduction and redox reaction of a Fe\(^{3+}/\text{Fe}^{2+}\) system. The estimated \( r_{et} \) is 2.17 Å for the redox reaction of Fe\(^{3+}/\text{Fe}^{2+}\) and 2.1–2.5 Å for the reduction of a proton, i.e., \( \text{H}^+ + e^- \rightarrow \text{H} \).

This result suggests that redox species are located near the compact layer (inner Helmholtz layer of ~2 Å thickness) formed on the electrode surface. Taking these situation into consideration, we assumed \( r_{et} = 3 \) Å for simplicity for the evaluation of the electron transfer integral \( v \).

Table 10 shows the values of electron transfer integral \( v \) obtained by \( k^0 \) method for the electrode reaction Eq. (R-1).

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}
\]  
(R-1)

As seen in Table 10, the evaluated electron transfer integral is very small. It is in the order of \( 10^{-5} - 10^{-3} \) eV. Table 11 shows the values of \( v \) calculated by \( i_0 \) method for the electrode reaction Eq. (R-1).

As seen in Table 11, the electron transfer integral \( v \) is very small, being in the order of \( 10^{-5} - 10^{-3} \) eV. Although the \( i_0 \) method is independent from the \( k^0 \) method, the obtained results of Tables 10 and 11 are close to each other. These results support the present theory.

We have also applied the present theory for the analysis of \( k^0 \) and \( i_0 \) values reported for the following 7 electrode reactions Eqs. (R-2)–(R-8).

\[
\text{Bi}^{3+} + 3e^- \rightarrow \text{Bi} \]  
(R-2)

\[
[\text{Fe}^{III}(\text{CN})_6]^{3-} + e^- \rightarrow [\text{Fe}^{II}(\text{CN})_6]^{4-}
\]  
(R-3)

\[
\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}_2
\]  
(R-4)
independent methods agree well with each other, as is seen in this electrode and the state density of the electron acceptor is weak.4,11

Table 12. Average values of the calculated electron transfer integral \( \nu \) for the electrode reaction Eqs. (R-1)-(R-8).

| No | \( \nu_i/\text{A cm}^{-2} \) | \( C/\text{mol dm}^{-3} \) | \( \nu/\text{eV} \) |
|----|----------------|----------------|----------------|
| 1  | \( 1.0 \times 10^{-3} \) | \( 1.0 \times 10^{-2} \) | \( 7.7 \times 10^{-5} \) |
| 2  | \( 5.0 \times 10^{-3} \) | \( 1.5 \times 10^{-2} \) | \( 1.4 \times 10^{-5} \) |
| 3  | \( 1.0 \times 10^{-3} \) | \( 1.0 \times 10^{-2} \) | \( 7.7 \times 10^{-4} \) |
| 4  | \( 5.0 \times 10^{-4} \) | \( 1.0 \times 10^{-2} \) | \( 5.5 \times 10^{-5} \) |
| 5  | \( 7.55 \times 10^{-5} \) | 0.1 | \( 2.1 \times 10^{-4} \) |
| 6  | \( 1.7 \times 10^{-4} \) | \( 1.0 \times 10^{-2} \) | \( 6.1 \times 10^{-5} \) |
| 7  | 0.38 | 1.0 | \( 1.5 \times 10^{-4} \) |
| 8  | \( 5.01 \times 10^{-3} \) | \( 1.5 \times 10^{-2} \) | \( 1.4 \times 10^{-4} \) |
| 9  | \( 5.26 \times 10^{-2} \) | 1.0 | \( 5.6 \times 10^{-5} \) |

\( \nu_{av}^{(a)} \) \( = 1.7 \times 10^{-4} \)

a) Average value of \( \nu \).
b) Method to evaluate the electron transfer integral \( \nu \).
c) Number of data (\( \nu_i \) or \( \nu \)) used for analysis.

\[
\begin{align*}
\text{In}^{3+} + 3e & \rightarrow \text{In} \quad \text{(R-5)} \\
\text{Zn}^{2+} + 2e & \rightarrow \text{Zn} \quad \text{(R-6)} \\
\text{Cd}^{2+} + 2e & \rightarrow \text{Cd} \quad \text{(R-7)} \\
\text{Ni}^{2+} + 2e & \rightarrow \text{Ni} \quad \text{(R-8)}
\end{align*}
\]

Equations (54) and (56) were used for the analysis of \( \nu \) and \( \nu_i \) values reported for the electrode reactions Eqs. (R-2)-(R-8). For this purpose, it was assumed that these reactions are weak coupling case, where the overlap between the state density of electrons in the metal electrode and the state density of the electron acceptor is weak.4,11

Table 12 summarizes the average values of the calculated electron transfer integral \( \nu \) together with the values of activation energy \( \Delta E \). In this table the average values of \( \nu \) and the value of activation energy \( \Delta E \) for the electrode reaction Eq. (R-1) are also listed. As is shown in this table, the magnitudes of the calculated electron transfer integral \( \nu \) are mostly in the order of \( 10^{-2}-10^{-5} \text{eV} \). It should be noted that the average values of \( \nu \) obtained by two independent methods agree well with each other, as is seen in this table. These results support our present theory.

Table 13. Analysis of the Standard Rate constant \( k_0 \) for the Electrochemical Reduction of Organic compounds by \( k_0 \) Method. Electrode is Hg.

| No | Compound | \( \Delta E/\text{eV} \) | \( k_0/\text{cm s}^{-1} \) | \( \nu/\text{eV} \) |
|----|----------|----------------|----------------|----------------|
| 1  | Naphthalene | 0.141 | 23 | \( 4.95 \times 10^{-3} \) |
| 2  | Anthracene | 0.133 | 27 | \( 6.60 \times 10^{-3} \) |
| 3  | Perylene | 0.136 | 20 | \( 4.19 \times 10^{-3} \) |
| 4  | Trans-Stilbene | 0.133 | 27 | \( 6.60 \times 10^{-3} \) |
| 5  | \( \alpha \)-Methyl-trans-stilbene | 0.175 | 5 | \( 4.46 \times 10^{-3} \) |
| 6  | m-Dinitrobenzene | 0.170 | 6.5 | \( 4.88 \times 10^{-3} \) |
| 7  | p-Dinitrobenzene | 0.198 | 2.2 | \( 4.92 \times 10^{-3} \) |
| 8  | Dibenzo-furan | 0.139 | 21 | \( 4.77 \times 10^{-3} \) |
| 9  | Dibenzo-thiophene | 0.154 | 12 | \( 4.84 \times 10^{-3} \) |
| 10 | p-Naphthoquinone | 0.180 | 4.6 | \( 4.77 \times 10^{-3} \) |

\( \nu_{av}^{(a)} \) \( = 4.70 \times 10^{-3} \)
a) Average value of \( \nu \). Values of \( k_0 \) are from Ref. 26.

6. Analysis of Standard Rate Constant for Electrochemical Reduction of Organic Compounds

Because the present theory is general, we applied it to the analysis of kinetic parameters reported for other electrochemical reactions.4,11

Table 13 shows the values of electron transfer integral \( \nu \) obtained by \( k_0 \) method for the electrochemical reduction of various organic compounds expressed by Eq. (R-9).4,11

Organic compound + e \rightarrow \text{Organic compound}^-

(R-9)

As is shown in Table, the magnitude of the electron transfer integral \( \nu \) is small, being in the order of \( 10^{-2} \text{eV} \). It is well known that for the electrochemical reductions of many aromatic hydrocarbons such as substituted anthracenes, pyrene and perylene, standard rate constants are unusually large. However, the magnitude of \( \nu \) for naphthalene, perylene, and anthracene is not so large, being in the order of \( 10^{-3} \text{eV} \), as is seen in this Table. Large \( k_0 \) values for the electrochemical reduction of anthracens and perylene might be explained by rather small \( \Delta E \) values of 0.1–0.2 eV. In order to confirm reliability of the present theory, we calculated theoretically from Eq. (56) the magnitude of the standard rate constants \( k_0 \) for the electrochemical reduction of various organic compounds in Table 13. In the theoretical calculation, the average value of the electron transfer integral \( \nu_{av} = 4.70 \times 10^{-3} \text{eV} \) was used as the value of \( \nu \) for organic compounds in Table 13.

The results of the theoretical calculation are shown in Table 14.4,11 As is shown in this Table, theoretically calculated \( k_0 \) values agree quantitatively with experimental \( k_0 \) values. As far as we know, there is no report of theoretical calculation of standard rate constant \( k_0 \), because there is no theory to calculate \( k_0 \). The present theory has enabled it. This result of Table 14 supports strongly our present theory.

7. Conclusion

7.1 Is tunneling mechanism correct for electron transfer at electrode-electrolyte interface?

Quantum mechanical tunneling mechanism for the electron transfer at electrode-electrolyte interface has been proposed and discussed for the electron transfer process by physical electrochemists for a long time.17,24–25 So far there has been no clear conclusion about the electron transfer mechanism at electrode-electrolyte interface.
Table 14. Experimental values of $k_0$ and theoretically calculated $k_0$ values.

| No | Org Compound    | $\Delta E$/eV | $k_0$/cm$^{-1}$s$^{-1}$ | $k_0$/cm$^{-1}$s$^{-1}$ |
|----|-----------------|---------------|-------------------------|-------------------------|
|    |                 | Experimental$^a$ | Theory$^b$              |                         |
| 1  | Naphthalene     | 0.141         | 23                      | 18.9                    |
| 2  | Anthracene      | 0.133         | 27                      | 25.9                    |
| 3  | Perylene        | 0.136         | 20                      | 23                      |
| 4  | Trans-Stilbene  | 0.133         | 27                      | 25.9                    |
| 5  | α-Methyl-trans-stilbene | 0.175        | 5                       | 5                       |
| 6  | m-Dinitrobenzene| 0.170         | 6.5                     | 6.03                    |
| 7  | p-Dinitrobenzene| 0.198         | 2.2                     | 2.01                    |
| 9  | Dibenzo[1,4]cyclooctadiene | 0.139      | 21                      | 20.4                    |
| 10 | Dibenzo[1,4]cyclooctadiene | 0.154      | 12                      | 11.3                    |
| 11 | p-Naphthoquinone| 0.180         | 4.6                     | 4.1                     |

$^a$ Experimental values of $k_0$.

$^b$ Theoretically calculated values of $k_0$/cm$^{-1}$s$^{-1}$.

However, the present results indicate clearly the presence of electron transfer integral $\nu$ for the electron transfer process at electrode-solution interface, although its magnitude is quite small. It contradicts the quantum mechanical tunneling mechanism, because the magnitudes of kinetic parameters such as $k_0$ and $i_0$ for most electrochemical reactions can be explained quantitatively by the ordinary quantum mechanical theory based on the Fermi’s Golden rule.

Present results deny the quantum mechanical tunneling mechanism for electrode process, but support the ordinary electron transfer mechanism due to the overlap of wave functions between the electrode and redox species.

7.2 Comparison with the quantum electrode theory by Russian school

As for the quantum theory of electrode kinetics, a theory by Dogonadze and Levich et al. (Russian school) is well known.\(^{1,2}\) In their theory of electrode kinetics, the current potential relation is Gaussian.\(^{1-3}\) Their theory predicts a maximum in the current overpotential plot. However such a maximum has never been observed experimentally in current overpotential plots.\(^{3}\) This Gaussian type current potential relation has been considered a serious defect in their theory.

However in the present theory current-overpotential relation is exponential and in the same form as Butler-Volmer equation, as is shown in Eqs. (10) and (30). This result is consistent with experimental observation and supports the present theory.

In the theory by Russian school, transfer coefficient $\alpha_0$ is expected to depend on the overpotential. However, in most electrochemical reactions, there is no variation of transfer coefficient $\alpha_0$ with overpotential.\(^{3}\)

In the present theory, there is no variation of transfer coefficient $\alpha_0$ with overpotential. Moreover, the magnitude of transfer coefficient $\alpha_0$ can be calculated theoretically, as was already shown.\(^{10}\) Thus defects contained in the quantum electrochemistry by Russian school are solved in the present theory.

7.3 Characteristic features of quantum electrochemistry

1. Current Overpotential relation is in the same form with Butler Volmer relation as in the classical electrochemistry.

2. There exist electron transfer distance and the electron transfer integral for the electron transfer at the electrode-electrolyte interface.

3. Transfer coefficient changes depending on ionic strength of the electrolyte solution. The magnitude of the transfer coefficient is calculated quantitatively by the potential screening theory based on the Debye-Hückel theory.

4. Information about the electron transfer distance $r_a$ is contained in the screening factor $\alpha$ as well as the electrostatic screening.\(^{15}\)

5. The magnitude of the exchange current density of hydrogen evolution can be calculated quantitatively by the Quantum electrochemistry.\(^{9}\)

6. The magnitude of the electron transfer integral $\nu$ can be evaluated theoretically from standard rate constant $k_0$ and the exchange current density $i_0$. Not only the magnitude of the exchange current density but also the magnitude of the standard rate constants $k_0$ can be calculated theoretically for various electrode reactions.

8. Since the present quantum electrochemistry corresponds well to the classical electrochemistry it is easy even for experimental electrochemists to learn the theory, if they learn the fundamental course of quantum mechanics.

Since most of these characteristic features are not present in the classical electrochemistry, present quantum electrochemistry is expected to develop new aspects in the electrochemistry and electrocatalysis especially from microscopic level.

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