© 2000 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 73, 297—305 (2000)

Quantum Mechanical Interpretation and Evaluation of Hydrogen Evolution at Metal Electrodes

Tadayoshi Sakata

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8502

(Received July 27, 1999)

The quantum mechanical theory of electrode reactions was applied to a hydrogen evolution reaction. The dependence of the activation energy of the hydrogen exchange current densities on the kind of electrode metal was explained well by this theory. The magnitude of the hydrogen exchange current densities and hydrogen overvoltages at various metal electrodes were evaluated theoretically. The calculated results and the dependency on the kind of metal were found to agree well quantitatively with the experimental values.

In recent years, electrochemical charge transfer processes have received considerable theoretical attention at the quantum mechanical and molecular level.[1—6]

Recent trends and the progress of quantum mechanical treatments in electrode kinetics were reviewed by S.H.Khan.[7] Rose and Benjamin developed a molecular model for an electron transfer reaction at a solution-electrode interface.[8] They calculated the solvent diabatic free energy curves for the reaction $Fe^{3+}+e^{-}\rightarrow Fe^{2+}$ by molecular dynamics using an umbrella sampling procedure. They were used to calculate the rate of electron transfer as a function of the electrode–solution potential difference in the electronically nonadiabatic region. The value of the activation energy at zero overvoltage was found to be 0.6 eV, which is in excellent agreement with the experimental value of 0.59 eV. The effect of an ion-electrode contact on the energetics of heterogeneous electron transfer was studied by a molecular dynamics simulation.[9] It was observed that the energetics of the reaction at the interface differs substantially from the energetics of the reaction in the bulk when the solvation shell of the ion undergoes large changes due to ion transfer from the bulk to the interface.

For electron transfer between an ion and a metal electrode, several authors have adapted the Anderson–Newns Hamiltonian.[6,10—14] Straus et al. studied the adiabatic heterogeneous electron transfer reactions between an ion in solution and a metal electrode.[15] They studied the electron transfer reaction of $Fe^{3+}+e^{-}\rightarrow Fe^{2+}$ at a Pt(111) surface. The adiabatic classical free energy curve for the reaction was computed using umbrella sampling and molecular dynamics generated by the adiabatic solution to an Anderson–Newns Hamiltonian. From the crossing point of the free energy curve, the activation free energy, $\Delta G^{\#} = 0.49$ eV, was found for the reaction $Fe^{3+}+e^{-}\rightarrow Fe^{2+}$ at the reversible potential. It agrees fairly well with the experimental result of 0.59 eV. The calculation showed that the solvent activation free energy barrier and thermodynamic driving force for the electron transfer process can be significantly affected by water quantization. Quantum solvent models were found to more accurately describe the actual physical system, suggesting that the classical simulations are not adequate to study electrochemical electron transfer reactions.[15]

In most theories concerning electron transfer at an electrode solution interface, the electronic transition probability is generally kept unevaluated, or is determined in terms of the Wentzel, Kramer, and Brillouin (WKB)tunneling probability.[16] Khan et al. first made a quantum mechanical computation of the electronic transmission coefficient for the electron transfer reaction between the platinum and a redox complex in a solution by using the time-dependent perturbation theory expression of the transmission coefficient, i.e. Fermi's golden rule.[16] At the reversible potential, transmission coefficient, $\varkappa = 7.2\times10^{-3}$, was found.[17]

Recently, the present author presented a quantum mechanical theory of electron transfer reactions at metal electrodes.[18] The electron transfer rates in this theory are expressed by Yomosa's electron transfer theory,[19] which is based on time dependent perturbation theory. In this theory the free electron theory was adopted for the electronic structure of the metal electrodes, and the distribution functions in Gerischer's theory[20] and Hopfield's theory[21] were used for the distribution functions of redox species near the electrode surface.[18] 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 classical electrochemistry. This theory explained well the volcano-shaped dependence of the hydrogen exchange current on the adsorption energy of hydrogen on various metals. In the present manuscript the author would like to improve the theory in order to interpret the activation energy of the exchange current density and the standard rate constant and to apply this theory to the hydrogen evolution reaction, the most fundamental and important electrode reaction to quantitatively evaluate the hydrogen exchange current densities at various metal electrodes and to establish a quantum mechanical mechanism and an interpretation for the hydrogen evolution reaction.

Results and Discussion

A. Exchange Current of Hydrogen Evolution by a Quantum Theory of Electrode Reaction. In a previous manuscript, hydrogen evolution at various metal electrodes was discussed. There, hydrogen evolution was ascribed to a typical weak coupling case, where the overlapping between the distribution function of the electron donor (metal electrode) and that of the electron acceptor (proton) is poor.[18]

In the weak coupling case, the exchange current for a cathodic electron transfer reaction at metal electrodes is given by quantum theory of the electrode reaction[18] as,

$$i_0^c = \frac{2\pi e}{\hbar} v^2 C_A \rho(E_f) \exp \frac{\varepsilon_0 - \Delta\varepsilon_{fi} + eV_{eq}}{kT}. \tag{1}$$

Here, parameter v represents the electron exchange integral of the electron transfer and $\rho(E_f)$ is the state density of the metal electrode at the Fermi level E_f. C_A represents the concentration of the electron acceptor. V_{eq} represents the equilibrium potential of the A/A$^-$ system. Parameter ε_0 represents the energy level that corresponds to the redox potential of A/A$^-$. $\Delta\varepsilon_{fi}$ represents the interaction energy of the redox species on the electrode surface at the electron transfer.[18] Since the hydrogen evolution reaction is a typical weak coupling case,[18] Eq. 1 can be used. Now, we define

$$I_0 = \frac{2\pi e}{\hbar} v^2 C_A \rho(E_f), \tag{2}$$

$$\Delta E = \varepsilon_0 - \Delta\varepsilon_{fi} + eV_{eq}. \tag{3}$$

By using Eqs. 1, 2, and 3, Eq. 1 is expressed as

$$i_0 = I_0 \exp - \frac{\Delta E}{kT}. \tag{4}$$

As shown in Eq. 4, ΔE of Eq. 3 represents the activation energy of the exchange current and the standard rate constant by quantum mechanical electrode theory. However, ΔE of Eq. 3 has a flaw for a simple one electron transfer reaction. For a simple one electron transfer reaction the following relation holds:

$$\varepsilon_0 = -eV_{eq}. \tag{5}$$

When Eq. 5 is used for Eq. 3,

$$\Delta E = -\Delta\varepsilon_{fi} \tag{6}$$

is obtained. Equation 6 shows that the activation energy of the exchange current and standard rate constant is negative for $\Delta\varepsilon_{fi} > 0$ and zero for $\Delta\varepsilon_{fi} = 0$. However, neither a negative nor a 0 activation energy has been reported, as far as we know. The magnitude of ΔE reported in the literature is around 1 eV, or less than 1 eV in most cases. These facts cannot be explained by the above theory.

In order to obviate this flaw, we improve the quantum mechanical theory of electron transfer at metal electrodes as follows.

B. Improved Theory of a Quantum Mechanical Electron Transfer Reaction at Metal Electrodes. Let's consider the following cathodic one electron transfer reaction at a metal electrode:

$$\mathrm{A} + \mathrm{e_{el}} \rightarrow \mathrm{A}^{-\bullet} \tag{7}$$

Here, A and $\mathrm{e_{el}}$ represent an electron acceptor molecule and an electron from the electrode, respectively. For the cathodic electron transfer of Eq. 7, the electron transfer rate (k_c) is expressed by Yomosa's electron transfer theory,[19] as described in the previous manuscript.[18]

$$k_C = \frac{2\pi}{\hbar} C_A v^2 \int_{-\infty}^{\infty} D_+(E) D_-(E) \mathrm{d}E. \tag{8}$$

Here $D_+(E)$ is the distribution function of the electron accepting states of the electron acceptor A that was introduced by Gerischer and Hopfield.[20,21]

$$D_+(E) = \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{(E - \varepsilon_0 - \lambda)^2}{4\lambda kT}. \tag{9}$$

Here, E represents the electron energy and ε_0 is the energy level corresponding to the redox potential of A/A$^{-\bullet}$. $D_+(E)$ of Eq. 9 corresponds to the state density of the unoccupied states of the electron acceptor A. In Eq. 8 $D_-(E)$ represents the distribution function of electrons in the electron donor. $D_-(E)$ corresponds to the state density of the occupied states of the electron donor. In the case of the cathodic reaction, the electrode metal is the electron donor. When the free electron theory is adopted for the electronic structure of the metal electrode, we can use

$$D_-(E) = \rho(E) f(E). \tag{10}$$

Here, $\rho(E)$ and $f(E)$ represent the state density of electrons in the metal electrode and the Fermi–Dirac distribution function, respectively. By using Eq. 10, Eq. 8 can be written as

$$k_C = \frac{2\pi}{\hbar} C_A v^2 \int_{-\infty}^{\infty} D_+(E) \rho(E) f(E) \mathrm{d}E. \tag{11}$$

Now let's consider the Fermi–Dirac distribution function $f(E)$,

$$f(E) = \frac{1}{1 + \exp \frac{E - E_f}{kT}}. \tag{12}$$

Here, E_f represents the Fermi energy of the metal electrode. For $E - E_f \geq 3kT$, $f(E)$ can be approximated well as a Boltzman distribution,

$$f(E) \approx \exp - \frac{E - E_f}{kT}. \tag{13}$$

This approximation corresponds to the weak coupling case in a previous manuscript.[18] Equation 13 means that thermally excited electrons contribute to the electrode reactions. Hereafter, we use this approximation. Since the distribution function, $D_+(E)$, shows a distribution of width of λ, it cannot represent well the discrete nature of an electron acceptor state. In order to emphasize the discrete nature of the electron acceptor state, we assume $D_+(E)$ to be as follows:

$$D_+(E) = \delta(E - E_a^0 + \Delta\varepsilon_{fi} + e\alpha\eta), \tag{14}$$

where E_a^0 represents the energy level of the unoccupied state of the electron acceptor that accepts an electron from the metal electrode in the electron transfer reaction of Eq. 7. $\Delta\varepsilon_{fi}$ in Eq. 14 is defined as

$$\Delta\varepsilon_{fi} \equiv \Delta\varepsilon_{int,f} - \Delta\varepsilon_{int,i}. \tag{15}$$

Here $-\Delta\varepsilon_{int,f}$ represents the interaction energy of $A^{-\bullet}$ with the electrode surface at the same instant as the electron transfer. Suffix f represents the final state of the electron transfer. $-\Delta\varepsilon_{int,i}$ represents the interaction energy of A with the electrode surface at the initial state of the electron transfer. Suffix i represents the initial state of the electron transfer. In Eq. 14, η represents the overpotential, defined as,

$$\eta = V - V_{eq}, \tag{16}$$

$$V_{eq} = V_0 + \frac{kT}{e}\ln\frac{C_{Ox}}{C_R}. \tag{17}$$

Here, V, V_{eq}, and V_0 represent the electrode potential, the equilibrium potential, and the redox potential of $A/A^{-\bullet}$, respectively. C_{Ox} and C_R represent the concentration of the oxidized and reduced species, respectively. Equation 17 represents the Nernst Equation in classical electrochemistry based on the transition state theory. In Eq. 14, α represents the shielding factor of the overpotential (η) by the solvent layer between the electrode surface and the A molecule. The shielding factor(α) was introduced into the theory because the imposed overpotential is shielded by ions and solvent molecules in the solvent electrolyte layer near to the electrode surface.[18] Under this assumption the electron transferred to the A molecule is assumed to feel a shielded electric field, $\alpha\eta$. Therefore, the electronic level E_a^0 shifts by $-e\alpha\eta$, because of the shielded potential. The idea of a shielded potential by electrolyte ions and solvent molecules resembles the idea of the electrostatic potential shielding by free electrons in metals.[38] Equation 14 represents that E_a^0 shifts by $-\Delta\varepsilon_{fi}$ by an interaction at the electrode surface and by $-e\alpha\eta$ due to the shielded potential. The energy level expressed by the delta function of Eq. 14 emphasizes the discrete nature of the electron acceptor state as well as the energy shift by the interaction at the electrode surface and by the shielded overpotential. Substitution of Eqs. 13 and 14 into Eq. 11 gives

$$\begin{aligned} k_C &= \frac{2\pi}{\hbar}C_A\nu^2\int_{-\infty}^{\infty}\delta(E - E_a^0 + \Delta\varepsilon_{fi} + e\alpha\eta)\rho(E)\exp - \frac{E - E_f}{kT}\mathrm{d}E \\ &= \frac{2\pi}{\hbar}C_A\nu^2\rho(E_a)\exp - \frac{E_a^0 - \Delta\varepsilon_{fi} - e\alpha\eta - E_f}{kT}. \end{aligned} \tag{18}$$

Here, we defined

$$E_a \equiv E_a^0 - \Delta\varepsilon_{fi} - e\alpha\eta. \tag{19}$$

Here E_a represents the energy level of the electron acceptor A, which includes the effect of the interaction energy of the redox species at the electrode surface and the shielded overpotential. Now, let's assume $\rho(E_a) = \rho(E_f)$, as was done in a previous manuscript.[18] We note that the following equation holds from Eq. 16:

$$E_f = -eV = -e(\eta + V_{eq}). \tag{20}$$

When $\rho(E_a) = \rho(E_f)$ and Eq. 20 is used for Eq. 18, we obtain

$$k_C = \frac{2\pi}{\hbar}C_A\nu^2\rho(E_f)\exp - \frac{E_a^0 - \Delta\varepsilon_{fi} + eV_{eq}}{kT}\cdot\exp - \frac{e(1-\alpha)}{kT}\eta. \tag{21}$$

By using relation $i = ek_C$ between the electric current i and k_C, we can write the cathodic current (i_c) in the following form:

$$i_C = i_C^0\exp - \frac{e(1-\alpha)}{kT}\eta, \tag{22}$$

where

$$i_C^0 = ek_C^0 = \frac{2\pi e}{\hbar}\nu^2 C_A\rho(E_f)\exp - \frac{E_a^0 - \Delta\varepsilon_{fi} + eV_{eq}}{kT}, \tag{23}$$

$$k_C^0 = \frac{2\pi}{\hbar}\nu^2 C_A\rho(E_f)\exp - \frac{E_a^0 - \Delta\varepsilon_{fi} + eV_{eq}}{kT}. \tag{24}$$

Equation 22 has the same form as the quantum mechanical Butler–Volmer equation,which was defined in the previous manuscript.[18]. i_C^0 and k_C^0 of Eqs. 23 and 24 represent the exchange current density and standard rate constant in the quantum mechanical form, respectively. Equations 23 and 24 have almost the same form as those derived in the previous manuscript.[18] Now we define

$$K_0 = \frac{2\pi}{\hbar}\nu^2 C_A\rho(E_f), \tag{25}$$

$$I_0 = eK_0 = \frac{2\pi e}{\hbar}\nu^2 C_A\rho(E_f), \tag{26}$$

$$\Delta E = E_a^0 - \Delta\varepsilon_{fi} + eV_{eq}. \tag{27}$$

By using Eqs. 25, 26, and 27, Eqs. 23 and 24 are written as

$$i_0^C = I_0\exp - \frac{\Delta E}{kT}, \tag{28}$$

$$k_C^0 = K_0\exp - \frac{\Delta E}{kT}. \tag{29}$$

Equations 28 and 29 show that the activation energy of the exchange current and the standard rate constant is given by the same (ΔE) of Eq. 27. Figure 1 illustrates the physical meaning of the activation energy ΔE of Eq. 27. ΔE of Eq. 27 resembles that of Eq. 3. ε_0 in Eq. 3 is replaced by E_a^0 in Eq. 27. E_a^0 represents a real quantum level, whereas ε_0 is a thermodynamically defined energy level that corresponds to the redox potential.

The activation energy (ΔE) of Eq. 27 expresses a clearer physical meaning than ΔE of Eq. 3. As was pointed out, ΔE of Eq. 3 becomes negative, or 0, for a simple one electron transfer reaction of Eq. 7. However, this flaw is obviated in this improved theory. Hereafter, we apply this theory for interpretating the exchange current ($i_{0,H}$) for hydrogen evolution.

C. Activation Energy of the Exchange Current for Hydrogen Evolution. Since $\Delta\varepsilon_{fi}$ in Eq. 27 represents the interaction energy on the electrode surface at the electron transfer reaction, ΔE is expected to depend on the adsorption energy of hydrogen at the final state of electron transfer.[18] As was assumed in the previous manuscript,[18] let's assume

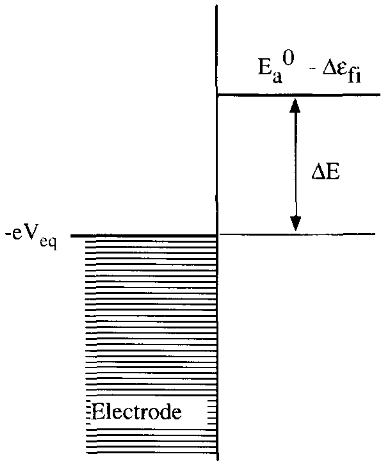

Fig. 1. Physical meaning of activation energy of exchange current and standard rate constant for cathodic electron transfer at metal electrode.

$$\Delta\varepsilon_{fi} = \beta E_{M-H}. \qquad (30)$$

Here E_{M-H} represents the adsorption energy of hydrogen on the metal surface in a vacuum and β represents the shielding factor of E_{M-H} by the solvent layer near to the electrode surface.[18] Under this assumption, Eq. 27 is written as

$$\Delta E = E_a^0 - \beta E_{M-H} + eV_{eq}. \qquad (31)$$

Equation 31 shows that the activation energy of the exchange current for hydrogen evolution changes depending on E_{M-H}, i.e. the adsorption energy of hydrogen on the metal surface.

The data of ΔE for the exchange current for hydrogen evolution $i_{0,H}$ can be found in the literature.[24—31]

Table 1 summarizes the data of ΔE from the literature.[24—31] The data of ΔE in Table 1 was plotted against E_{M-H}. The result is shown in Fig. 2. As for parameter *b*, $\beta = 0.40$ was obtained previously from an analysis of the E_{M-H} dependence of log $i_{0,H}$ on various kinds of metal electrodes based on the quantum theory of electrode reactions.[18] The solid line in Fig. 2 shows a line with a slope of $\beta = 0.40$. As shown in Fig. 2, the literature data of ΔE are approximately on this line. Thus, the result of Fig. 2 can be explained well by Eq. 31 with $\beta = 0.40$ based on the quantum theory of electrode reactions. Since the intercept at $E_{M-H} = 0.0$ eV in Fig. 2 is 1.3 eV, Eq. 31 yields

$$E_a^0 + eV_{eq} = 1.3 \text{ eV}. \qquad (32)$$

Table 1. The Activation Energy of Exchange Current of Hydrogen Evolution at Various Metal Electrodes

Metal	E_{M-H}/eV	ΔE/eV	Ref.
Cu	1.86	0.48	25
Ni	1.97	0.435	24
Pt	2.6	0.304	31
Ga	1.60	0.77	29
In	1.33	0.61	26
Hg	1.26	0.78	28
Re	2.61	0.26	30
Pd	2.54	0.413	28

D. Theoretical Evaluation of the Electron Exchange Energy for Hydrogen Evolution. Equation 28 gives

$$I_0 = i_{0,H} \exp \frac{\Delta E}{kT}. \qquad (33)$$

When the experimental values for $i_{0,H}$ and ΔE were used for Eq. 33, the I_0 values were calculated by Eq. 33 for 8 kinds of metal electrodes in Table 1. The calculated values of I_0 are given in Table 2. Equation 26 gives

$$v^2 = \frac{\hbar}{2\pi e} \frac{I_0}{C_A \rho(E_f)}. \qquad (34)$$

Equation 34 indicates that the electron exchange energy (v) for hydrogen evolution can be calculated from the values I_0, C_A, and $\rho(E_f)$. The proton concentration in the experiments to measure the exchange current density for hydrogen evo-

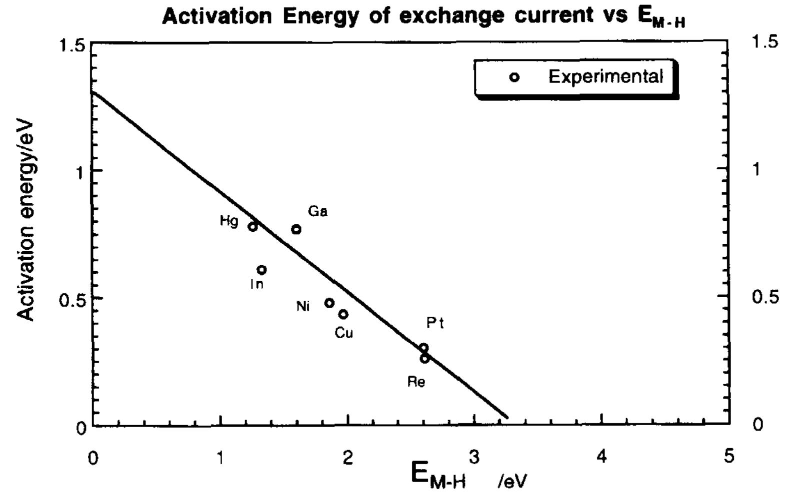

Fig. 2. Activation energy ΔE of hydrogen exchange current on several metal electrodes plotted against the adsorption energy of hydrogen on metal E_{M-H}. The data of E_{M-H} are from Krishtalik.[32,36] The adsorption energy of hydrogen on Pd was estimated from the heat of adsorption.[33,36]

Table 2. Calculated Values of I_0 and Experimental Values of ΔE and $\log i_{0,\mathrm{H}}$

Metal	ΔE/eV	$\log i_{0,\mathrm{H}}$	I_0/A cm^{-2}
Cu	0.48	−7.8	1.84
Ni	0.435	−5.25	114.35
Pt	0.304	−3.0	128.05
Ga	0.77	−9.4	3439.0
In	0.61	−10.4	0.705
Hg	0.78	−12.3	6.37
Re	0.26	−3.0	23.34
Pd	0.413	−3.1	6896.5

lution is mostly 0.1—1.0 M (1 M = 1 mol dm^{-3}).[34] Let's use as C_A value of

$$C_A = 3.0 \times 10^{20}\ \mathrm{cm}^{-3}. \tag{35}$$

$C_A = 3.0\times10^{20}$ cm^{-3} corresponds to a proton concentration of 0.5 M. The state density, $\rho(E_f)$, for various metals was already calculated based on the electronic heat capacity of various metals in the previous manuscript.[18] By using the $\rho(E_f)$ values of Table 1 in the revious manuscript,[18] $C_A = 3.0\times10^{20}$ cm^{-3} and I_0 in Table 2, we can calculate the electron exchange energy (v) for hydrogen evolution at 8 kinds of metal electrodes. The results are given in Table 3. As shown in Table 3, the calculated values of the electron exchange energy (v) for hydrogen evolution are very small. They are from 10^{-5} cm^{-1} to 10^{-4} cm^{-1}. In the previous manuscript it was concluded that the rate determining step of the hydrogen evolution is the following electron transfer on the metal electrodes for $E_{\mathrm{M-H}} < 2.6$ eV:[18]

$$\mathrm{H}^+ + \mathrm{e} \rightarrow \cdot\mathrm{H}. \tag{36}$$

Eight kinds of metals in Table 3 belong to this group where the rate determining step of hydrogen evolution is the electron transfer of Eq. 36. Therefore, the electron exchange energy (v) for hydrogen evolution in Table 3 represents the magnitude of the electron exchange interaction for the electron transfer reaction of Eq. 36 on the electrode surface.

From the electron exchange energy (v), we can evaluate the transition rate (k_{et}) of electron transfer for the electrode reaction of Eq. 36. The electron transfer rate (k^0_{et}) can be evaluated by Fermi's golden rule,

$$k^0_{\mathrm{et}} = \frac{2\pi}{\hbar} v^2 \rho_f(E), \tag{37}$$

where ρ_f(E) represents the state density of the final state of the electron transfer. Since each vibronic level at the final state of the electron transfer splits by v because of the electron exchange interaction, we may approximate

$$\rho_f(E) \cong \frac{1}{v}. \tag{38}$$

Under this approximation, Eq. 37 gives

$$k^0_{\mathrm{et}} = \frac{2\pi v}{\hbar}. \tag{39}$$

k^0_{et}, defined by Eq. 39, is thought to represent the electron transfer rate of a pure electronic process.

The transition time of electron transfer (τ^0_{et}) is defined from Eq. 39 as

$$\tau^0_{\mathrm{et}} \equiv \frac{1}{k^0_{\mathrm{et}}} = \frac{\hbar}{2\pi v} = \frac{2\pi v}{\hbar}. \tag{40}$$

By using the v values given in Table 3, we can calculate the transition time (τ^0_{et}) of electron transfer at 8 metal electrodes by using Eq. 40. Table 4 gives the calculated electron transfer time (τ^0_{et}) at 8 kinds of metal electrodes. As seen in this Table 4, τ^0_{et} is on the order of 10^{-9} s to 10^{-8} s. As can be seen in Eq. 29, the rate constant (k^0_{C}) has the factor of $\exp -\frac{\Delta E}{kT}$. The factor $\exp -\frac{\Delta E}{kT}$ is considered to represent the effect of thermal excitation of electrons on the electron transfer process. The transition time (τ^0_{et}) is considered to represent the electron transfer time by a pure electronic process without thermal activation for the electrode reaction of Eq. 36.

E. Theoretical Evaluation of the Exchange Current ($i_{0,\mathrm{H}}$) for Hydrogen Evolution at Various Metal Electrodes. Equations 26, 27, and 28 show that the exchange current ($i_{0,\mathrm{H}}$) for hydrogen evolution at various metal electrodes can be calculated once the magnitudes of 4 parameters C_A, v, $\rho(E_f)$, and ΔE are known.

We use Eq. 35 as the C_A value. As the exchange energy (v), the average value of v for 8 kinds of metal electrodes given in Table 3 is used. The average value of v for 8 kinds of metal electrodes is calculated as

$$v = 3.888 \times 10^{-20}\ \mathrm{erg}. \tag{41}$$

The values of $\rho(E_f)$ in Table 1, calculated in the previous manuscript[18] are used as the state density of each metal electrode at the Fermi level $\rho(E_f)$. Thus, I_0 is calculated at

Table 3. Calculated Values of Exchange Energy v for Hydrogen Evolution and I_0 and $\rho(E_f)$ Used for the Calculation

Metal	I_0/A cm^{-2}	$\rho(E_f)^{a)}$	v/10^{-20} erg	v/10^{-5} cm^{-1}
Cu	1.84	1.86	0.588	2.96
Ni	114.35	18.7	1.463	7.37
Pt	128.05	18.2	1.569	7.90
Ga	3439.0	1.59	27.51	138.51
In	0.705	4.51	0.234	1.18
Hg	6.37	4.78	0.683	3.44
Re	23.34	6.14	1.153	5.81
Pd	6896.5	25.2	9.787	49.27

a) The unit of $\rho(E_f)$ is 10^{11} erg^{-1} molecule^{-1}. The values of $\rho(E_f)$ are from Ref. 18.

Table 4. Transition Time of Electron Transfer τ_{et} Calculated by Eqs. 31,39,40, and Electron Exchange Energy v

Metal	v/10^{-5} cm^{-1}	τ_{et}/10^{-9} s
Cu	2.96	28.6
Ni	7.37	11.5
Pt	7.90	10.7
Ga	138.5	0.6
In	1.18	71.6
Hg	3.44	24.6
Re	5.81	14.6
Pd	49.27	1.7

various metal electrodes from Eq. 26 by using v of Eq. 41, C_A and $\rho(E_f)$.

To calculate the exchange current ($i_{0,H}$) for hydrogen evolution at various metal electrodes, the activation energy of the exchange current ΔE should be evaluated. Equations 31 and 32 and $\beta = 0.4$ yield

$$\Delta E = E_a^0 - \beta E_{M-H} + eV_{eq} = 1.3 - 0.4E_{M-H}. \qquad (42)$$

Equation 42 shows that the activation energy of the exchange current (ΔE) can be calculated from the adsorption energy of a hydrogen atom (E_{M-H}) on various metals.[32] Once the parameters and ΔE and I_0 are known, the exchange current ($i_{0,H}$) for hydrogen evolution at various metal electrodes can be calculated by Eq. 28. We have calculated the exchange current $i_{0,H}$ for hydrogen evolution at various metal electrodes by this method. Table 5 gives the calculated values of $\log i_{0,H}$ together with I_0, E_{M-H}, and ΔE. Although the agreement between the theoretically evaluated $\log i_{0,H}$ and the experimental ones is bad for Ti, Cr, Nb, Mo, and W, it is unbelievably good for Fe, Co, Ni, Cu, Zn, Ga, Ag, Cd, In, Sn, Au, Hg, Tl, Pb, and Bi, as is shown in Table 5. Figure 3 shows the theoretically evaluated $\log i_{0,H}$ (Theory) and the experimental $\log i_{0,H}$ (Expt.) plotted against E_{M-H}, i.e. the adsorption energy of hydrogen atom on metal. As shown in this Fig. 3, the agreement between theory and experiment is quite good for metals with $E_{M-H} < 2.6$ eV. However, the discrepancy between theory and experiment increases for metal electrodes with $E_{M-H} > 2.6$ eV. This result agrees well with the conclusion obtained in the previous manuscript that the rate determining step of hydrogen evolution is the

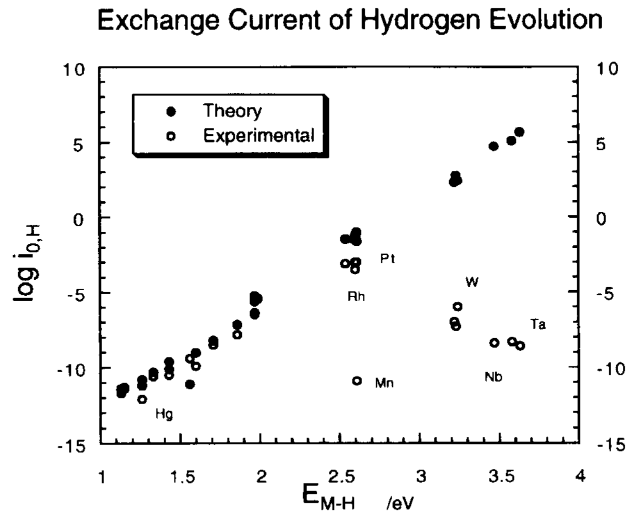

Fig. 3. Calculated hydrogen exchange current $\log i_{0,H}$ (Theory) and experimental values of hydrogen exchange current $\log i_{0,H}$ (Expt) at various metal electrodes[34] plotted against E_{M-H}.[32]

Table 5. Calculated Values of Hydrogen Exchange Current $\log i_{0,H}$ (Theory) and Experimental Values of Hydrogen Exchange Current $\log i_{0,H}$ (Expt) at Various Metal Electrodes[34] Together with E_{M-H}/eV, I_0/A cm^{-2}, and ΔE/eV

Metal	E_{M-H}/eV[a)]	I_0/A cm^{-2}	ΔE/eV	$\log i_{0,H}$ (Theory)	$\log i_{0,H}$ (Expt)
Ti	3.58	737.8	−0.132	+5.09	−8.3
Cr	3.22	308.7	0.012	+2.29	−7.0
Mn	2.61	2030.2	0.256	−0.99	−10.9
Fe	1.97	1097.6	0.512	−5.56	−5.65
Co	1.99	1048.1	0.504	−5.45	−5.4
Ni	1.97	1543.3	0.512	−5.41	−5.25
Cu	1.86	153.5	0.556	−7.16	−7.83
Zn	1.43	141.1	0.728	−10.1	−10.5
Ga	1.60	131.2	0.66	−9.0	−9.9
Nb	3.47	1716.6	−0.088	+4.71	−8.4
Mo	3.23	440.7	0.008	+2.75	−7.3
Rh	2.60	1081.1	0.26	−1.33	−3.5
Pd	2.54	2079.8	0.284	−1.45	−3.1
Ag	1.71	142.0	0.616	−8.20	−8.5
Cd	1.26	151.9	0.796	−11.2	−11.2
In	1.33	372.2	0.768	−10.3	−10.6
Sn	1.43	392.0	0.728	−9.6	−9.6
Pt	2.60	1502.0	0.260	−1.20	−3.0
Au	1.97	190.9	0.512	−6.4	−6.5
Ta	3.63	1303.9	−0.152	+5.67	−8.6
W	3.24	286.4	0.004	+2.39	−6.0
Re	2.61	506.7	0.256	−1.60	−3.0
Ir	2.60	683.3	0.260	−1.53	−3.0
Hg	1.26	394.5	0.796	−10.8	−12.1
Tl	1.13	323.5	0.848	−11.7	−11.4
Pb	1.15	627.2	0.840	−11.3	−11.4
Bi	1.56	1.7	0.676	−11.1	−9.4

a) The most data of E_{M-H} are from Krishtalik.[32] E_{M-H} values for Cr, Pd, and Mn were estimated from heat of chemisorption of hydrogen.[33,36]

electron transfer of Eq. 36 for metal electrodes whose $E_{\mathrm{M-H}}$ is smaller than 2.6 eV, whereas it is not the electron transfer, but the recombination of hydrogen for those metal electrodes whose $E_{\mathrm{M-H}}$ is larger than 2.6 eV. Therefore, large discrepancy between theory and experiment observed for Ti, Cr, Nb, Mo, and W is reasonable, because the rate determining step is not the electron transfer of Eq. 36 for these metal electrodes. For $E_{\mathrm{M-H}} > 2.6$ eV, ΔE becomes smaller than 0.26 eV. This means that the approximation of the weak coupling case does not hold well for $E_{\mathrm{M-H}} > 2.6$ eV. This might be another reason for the discrepancy.

The good agreement between theory and experiment observed for Fe, Co, Ni, Cu, Zn, Ga, Ag, Cd, In, Sn, Au, Hg, Tl, Pb, and Bi is reasonable, because $E_{\mathrm{M-H}}$ is smaller than 2.6 eV and the rate determining step is electron transfer of Eq. 36 for these metal electrodes. As shown in Table 5 and Fig. 3, the agreement between theory and experiment is not very good for Mn, Rh, Pd, Re, and Pt. $E_{\mathrm{M-H}}$ for these metals is close to 2.6 eV. $E_{\mathrm{M-H}}$ for these metals is located at the transition region between the weak $E_{\mathrm{M-H}}$ ($E_{\mathrm{M-H}} < 2.6$ eV) and the strong $E_{\mathrm{M-H}}$ ($E_{\mathrm{M-H}} > 2.6$ eV) region. This result suggests that the rate determining step on these metal electrodes is not pure electron transfer, but is affected by hydrogen adsorption. All of the above results support the present theory and indicate the important role of the adsorptive interaction of atomic hydrogen on the electrode surface, i.e., $\Delta\varepsilon_{\mathrm{fi}} > 0$ at the final state of electron transfer.

Table 6 gives a classification of metal electrodes according to the electrocatalytic activity of hydrogen evolution. From the above discussions, various metal electrodes can be classified into 3 groups, depending on the magnitude of the adsorption energy of hydrogen, i.e.$E_{\mathrm{M-H}}$.

F. Importance of Electron Transfer Adsorption of Atomic Hydrogen on the Electrode Surface at the Final State of Electron Transfer. In the present theory, the activation energy (ΔE) as well as the electron exchange energy play important roles in the exchange current, as can be seen in Eqs. 23, 28, and 30. As assumed in Eqs. 30 and 31, ΔE is determined mainly by the magnitude of $E_{\mathrm{M-H}}$. Equation 30 means that the adsorption energy of hydrogen is weakened by a solvent layer on the electrode surface approximately by $\beta = 0.4$. This means that atomic hydrogen interacts with the electrode surface, and is stabilized by $\beta E_{\mathrm{M-H}}$ at the final state of the electron transfer. In the previous manuscript we called this interaction as electron transfer adsorption. The electrode reaction of hydrogen evolution is explained well by the concept of electron transfer adsorption as shown above.

G. Theoretical Evaluation of Hydrogen Overvoltage. For the hydrogen evolution reaction, the following Butler–Volmer type equation holds in the weak coupling case:[18]

$$i = i_{0,\mathrm{H}} \exp - \frac{e(1-\alpha)}{kT}\eta, \tag{43}$$

where η represents the overvoltage. Equation 43 gives

$$\eta_{\mathrm{H}} = \frac{2.3kT}{e(1-\alpha)}\{\log i_{0,\mathrm{H}} - \log i\}, \tag{44}$$

where η_{H} represents the hydrogen overvoltage. If $\alpha = 0.5$ and $i = 10^{-3}$ A cm^{-2} are assumed in Eq. 44, the hydrogen overvoltage (η_{H}) at 10^{-3} A cm^{-2} can be expressed at $T = 300$ K as

$$\eta_{\mathrm{H}} = 0.11891\,\{3.0 + \log i_{0,\mathrm{H}}\}. \tag{45}$$

When the theoretically calculated $\log i_{0,\mathrm{H}}$ values in Table 5 are used in Eq. 45, the hydrogen overvoltage (η_{H}) at 10^{-3} A cm^{-2} can be calculated for various metal electrodes. The result is given in Table 7. In the same table the experimental values of η_{H} reported in Ref. 35 are given for a comparison. As shown in this Table 7, the agreement between theory and experiment is quite satisfactory. This supports our present model.

In the above calculation, $\alpha = 0.5$ was assumed. For a gold electrode, $\alpha = 0.163$ was reported by Pentland et al.[37] When $\alpha = 0.163$ is used in Eq. 21, $\eta_{\mathrm{H}} = -0.242$ V is obtained. The theoretical value of η_{H} for the Au electrode listed in Table 5 is -0.438 V for $\alpha = 0.5$. $\eta_{\mathrm{H}} = -0.242$ V is much closer to the experimental value of $\eta_{\mathrm{H}} = -0.12$ V compared with $\eta_{\mathrm{H}} = -0.40$ V for $\alpha = 0.5$. This example indicates that the value of α has a strong influence on evaluating the hydrogen

Table 6. Classification of Various Metal Electrodes According to Electroanalysis of Hydrogen Evolution

Group	$E_{\mathrm{M-H}}$	r.d.s.[a] of hydrogen evolution	$\log i_{0,\mathrm{H}}$	η_{H}[b]	Metal
A	Weak $E_{\mathrm{M-H}} < 2.5$ eV	Electron transfer of $H^+ + e \rightarrow H\cdot$	$-12.1 \leq \log i_{0,\mathrm{H}} \leq -5.0$	Large	Fe,Co,Ni,Cu, Zn,Ga,Ag,Cd, In,Sn,Au,Hg, Tl,Pb,Bi,
B	Intermediate $E_{\mathrm{M-H}} \approx 2.6$ eV	Electron transfer affected by H-adsorption	$\log i_{0,\mathrm{H}} \approx -3.0$	Small	Pt,Ir,Re,Rh, Pd
C	Strong $E_{\mathrm{M-H}} > 2.6$ eV	Recombination of H· $H\cdot + H\cdot \rightarrow H_2$	$\log i_{0,\mathrm{H}} \leq -7.0$	Large	Ti,Cr,Mn, Nb,Mo,Ta, W,Cr

a) r.d.s. : Rate determining step. b) η_{H} : Hydrogen overvoltage.

Table 7. Calculated and Experimental Values of Hydrogen Overvoltage η_H for Various Metal Electrodes

Metal	$\log i_{0,H}$ (Theory)	Calcd η_H/V	Expt η_H/V[a)]
Cu	−7.16	−0.495	−0.46—−0.57
Ga	−9.0	−0.713	−0.68
Ag	−8.20	−0.618	−0.59
Cd	−11.2	−0.98	−0.99
In	−10.3	−0.87	−0.80
Fe	−5.56	−0.30	−0.40
Ni	−5.41	−0.29	−0.32—−0.33
Pt	−1.20	+0.21	−0.01—−0.27
Au	−6.4	−0.40	−0.12
Hg	−10.8	−0.93	−1.03—−1.04
Tl	−11.7	−1.03	−0.61—−1.05
Pb	−11.3	−0.99	−0.85
Pd	−1.45	+0.184	−0.01—−0.09

a) Experimental values of hydrogen overvoltage η_H are from Ref. 35.

overvoltage. From this point of view, Eq. 45 used in the present calculation is not a good equation. If we can use in Eq. 44 the experimental values of α that is determined at the potential where the hydrogen overvoltage was measured, the theoretical values of η_H in Table 7 would be improved more.

H. Quantum Mechanical Picture of Electron Transfer for Hydrogen Evolution at Metal Electrodes. From the above results, we can draw a schematic picture that illustrates the quantum mechanical electron transfer for hydrogen evolution, i.e. Eq. 36. Figure 4 shows a schematic picture of electron transfer for hydrogen evolution at a metal electrode. Electrons near to the Fermi level of the metal electrode are excited by the thermal energy (kT). Electron transfer occurs from these thermally excited electrons to the electron accepting states (unoccupied states) of protons near to the electrode surface at $E_a^0 - \Delta\varepsilon_{fi}$ with a very small electron exchange energy, $v \approx 10^{-5}$—10^{-3} cm^{-1} (see Table 3). This electron transfer takes place equi-energetically according to Fermi's golden rule. The transition time of the electron transfer is 10^{-9}—10^{-8} s, depending on the magnitude of v, as shown in Table 3. Hydrogen atoms produced at the final state of the electron transfer interact with the electrode surface and are stabilized by $E_{M-H} \approx 0.4E_{M-H}$ through this adsorptive interaction. Since this ineraction energy depends on the kind of metal, the magnitude of the hydrogen exchange current depends on the kind of metal as shown in Eqs. 27, 28, and 30. Figure 4 also illustrates the concept of electron transfer adsorption at the final state of the electron transfer. The electron transfer adsorption at the final state of the electron transfer for hydrogen evolution is a dynamic interaction. Such a dynamic ineraction on the electrode surface cannnot be treated by the classical theory of electrode reactions based on the transition state theory. As was explained in the above discussion, such a dynamic interaction as well as the magnitude of the electron transfer rate can be explained well by the quantum mechanical theory of electrode reactions.

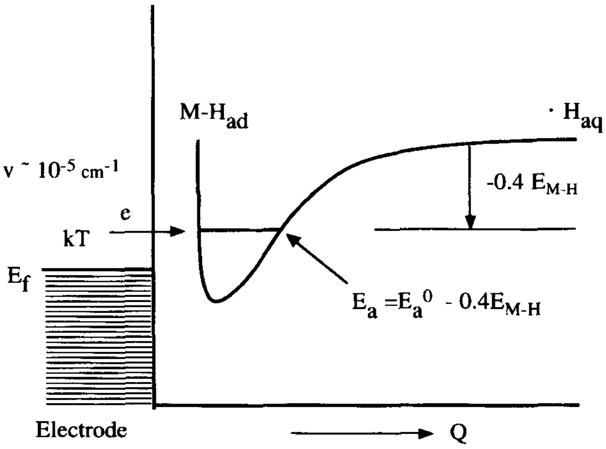

Fig. 4. A Schematic picture of electron transfer for hydrogen evolution at a metal electrode.

The author thanks Mr. H. Nakamura for carrying out the experiments of the activation energies of the hydrogen exchange currents at several metal electrodes and confirming the reproducibility of the values reported in the past literature.

References

1 R. R. Dogonadze, in "Reactions of Molecules at Electrodes," ed by N. Hush, Wiley, London (1971), p. 135.

2 W. Schmickler, *J. Electroanal. Chem.*, **204**, 31 (1986).

3 K. L. Sebastian and P. Ananthapadmanabhan, *J. Electroanal. Chem.*, **230**, 43 (1987).

4 A. M. Kuznetsov, *J. Electroanal. Chem.*, **241**, 45 (1988).

5 A. V. Gorodyskii, A. I. Karasevskii, and D. V. Matyushov, *J. Electroanal. Chem.*, **315**, 9 (1988).

6 B. B. Smith and J. T. Hynes, *J. Chem. Phys.*, **99**, 6517 (1993).

7 S. U. M. Khan, "Modern Aspects of Electrochemistry, Number 32," ed by J. O'M. Bockris, Prenum Press, New York (1997), p. 71.

8 D. A. Rose and I. Benjamin, *J. Chem. Phys.*, **100**, 3545 (1994).

9 X. Xia and M. L. Berkowitz, *Chem. Phys. Lett.*, **227**, 561 (1994).

10 W. Schmickler, *Chem. Phys. Lett.*, **237**, 152 (1995).

11 O. Pecina, W. Schmickler, and E. Sphor, *J. Electroanal. Chem.*, **394**, 29 (1995).

12 P. W. Anderson, *Phys. Rev.*, **124**, 41 (1961).

13 D. M. Newns, *Phys. Rev.*, **178**, 1123 (1969).

14 K. L. Sabastian, *J. Chem. Phys.*, **99**, 5056 (1989).

15 J. B. Straus, A. Calboun, and G. A.Voth, *J. Chem. Phys.*, **102**, 529 (1995).

16 J. O'M. Bockris and S. U. M. Khan, "Quantum Electrochemistry," Prenum Press, New York (1979).

17 S. U. M. Khan, P. Wright, and J. O'M. Bockris, *Elektrokhimiya*, **13**, 914 (1977).

18 T. Sakata, *Bull. Chem. Soc. Jpn.*, **69**, 2435 (1996).

19 S. Yomosa, *J. Phys. Soc. Jpn.*, **35**, 1501 (1973).

20 H. Gerischer, *Photochem. Photobiol.*, **16**, 243 (1972).

21 J. J. Hopfield, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 3640 (1974).

22 J. Goodisman,"Electrochemistry: Theoretical Foundations," John Wiley & Sons, New York (1987), p. 39.

23 A. J. Bard and L. R. Faulkner, "Electrochemical Methods," John Wiley & Sons, New York (1980).

24 B. E. Conway, E. M. Beatty, and P. A. D. DeMaine, *Elec-*

trochim. Acta, **7**, 39 (1962).

25 J. O'M. Bockris and N. Pentland, *Trans. Faraday Soc.*, **48**, 833 (1952).

26 J. Butler and M. Dienst, *J. Electrochem. Soc.*, **112**, 226 (1965).

27 B. Post and C. F. Hiskey, *J. Am. Chem. Soc.*, **72**, 4203 (1950).

28 M. Maeda, "Chemistry of Electrode," Gihodo Publishing, Tokyo (1959).

29 J. N. Butler and M. L. Meehan, *Trans. Faraday Soc.*, **62**, 3524 (1966).

30 M. J. Joncich, L. S. Stewart, and F. A. Posey, *J. Electrochem. Soc.*, **112**, 217 (1965).

31 F. P. Bowden, *Proc. R. Soc. (London)*, **126a**, 107 (1929).

32 L. I. Krishtalik, *Adv. Electrochem. Electrochem. Eng.*, **7**, 283 (1970).

33 F. C. Tompkins, "Chemisorption of Gases on Metals," Academic Press, London (1978).

34 S. Trasatti, *J. Electroanal. Chem.*, **39**, 163 (1972).

35 P. Rüetschi and P. Delahay, *J. Chem. Phys.*, **23**, 195 (1955).

36 I. Toyoshima and G. A. Somorjai, *Catal. Rev. -Sci. Eng.*, **19** (**1**), 105 (1979).

37 N. Pentland, J. O'M. Bockris, and E. Sheldon, *J. Electrochem. Soc.*, **104**, 182 (1957).

38 C. Kittel, "Introduction of Solid State Physics," John Wiley & Sons, Inc., New York (1986).