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Quantum Mechanical Theory of Electron Transfer Reactions at Metal Electrodes

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The quantum theory of electron transfer reactions at metal electrodes was studied. The obtained potential dependence of the electron transfer rate in the weak coupling case resembles the Butler–Volmer equation of classical electrochemistry. The volcano-shaped dependence of the hydrogen exchange current on the adsorption energy of hydrogen on various metals was explained microscopically, based on this theory. The mechanism of hydrogen evolution was also explained microscopically based on this theory. The exchange current density for hydrogen evolution at Pt electrode calculated quantitatively agreed well with the experimental value.

The general theory that is adapted commonly for electrode kinetics is the activated complex theory based on the transition state theory.[1] Although this theory has been applied successfully to electrode kinetics to describe the basic features, it is a phenomenological theory that is not based on the quantum theory. Therefore it can not describe the electron transfer process at electrodes from the microscopic view point.

Major contributions to the microscopic basis for electron transfer processes have been made by R. Marcus,[2] Hush,[3] Levich,[4] Dogonadze,[5] Gerischer,[6] and others.[7,10] In these theories the distribution of electronic states of redox species is given in a Gaussian from.[4,6,10] In many current theories, a phenomenological frequency factor is used for the electron transfer rate instead of electron exchange energy. The difference just corresponds to the problem of adiabatic or non adiabatic process. The concept of distribution function is widely accepted in semiconductor-photoelectrochemistry.[4,6] When Levich's theory is applied to electrode reactions at metal electrode, the obtained current potential relation is also Gaussian.[4] However, the experimental current potential relation universally observed in electrode-kinetic experiment free of transport control is exponential. The Gaussian current potential relation yields $d\alpha/d\eta\neq0$, here α is transfer coefficient and η is overpotential. In Dogonadze's quantum theory of molecular electrode kinetics, transfer coefficient also varies depending on η.[5] However, there is no variation of transfer coefficient, α, with overpotential, η, in most electrochemical reactions.[8] This is inconsistent with observation. In order to solve this difficulty, Bockris et al. proposed a Boltzman distribution for electronic states in solution.[8]

In the present paper I would like to propose a quantum-mechanical theory of electron transfer reactions at metal electrodes and show that a Butler–Volmer type (exponential) current potential relation can be derived in the weak coupling case from the Gaussian distribution of electronic states of redox species. This theory is successfully applied to hydrogen evolution reaction and the molecular mechanism is discussed from a microscopic viewpoint.

Theory

A) Cathodic Process. Let's consider the following cathodic reaction at a metal electrode.

$$\mathrm{A}+\mathrm{e}_{\mathrm{el}}\rightarrow \mathrm{A}^{-\bullet} \tag{1}$$

Here A represents an electron acceptor molecule near the electrode surface in the solution and e_{el} represents an electron from the metal electrode.

For the above cathodic electron transfer from the electrode to the electron acceptor, the electron transfer rate k_{C} is expressed by Yomosa's electron transfer theory,[9] as follows,

$$k_{\mathrm{C}}=\frac{2\pi}{\hbar}C_{\mathrm{A}}v^2\int_{-\infty}^{+\infty}D_{+}(E)D_{-}(E)\mathrm{d}E \tag{2}$$

The from of Eq. 2 resembles the theory of semiconductor electrode of Gerischer,[6] electron transfer theory of Levich,[4] and electron transfer theory of Hopfield.[10]

In Eq. 2 C_{A} is the concentration of electron acceptor molecules near the electrode and $D_{+}(E)$, $D_{-}(E)$, v, $\rho(E)$, and $f(E)$ represent the following:

$D_{+}(E)$: Distribution function of an electron acceptor in solution. It is called electron insertion spectrum.[10]

$D_{-}(E)$: Distribution function of an electron in the electron donor. It is called electron removal spectrum.[10]

v: the electron exchange integral of an electron acceptor with free electrons of the metal electrode at the electrode.[4]

In the cathodic reaction at an electrode, the metal electrode works as an electron donor. For the electronic structure of the metal, the free electron theory[11] is adopted for simplicity. Under this condition, for $D_{-}(E)$

$$D_-(E) = \rho(E)f(E) \qquad (3)$$

can be used.4)

Here,

$\rho(E)$: State density of metal electrode

$f(E)$: Fermi–Dirac distribution function

The Fermi–Dirac distribution function is

$$f(E) = \frac{1}{1 + \exp\frac{E-E_\mathrm{f}}{kT}} \qquad (4)$$

Here, E_f represent Fermi energy and k is Bolzmann constant. By using Eq. 3, we can write Eq. 2 as,

$$k_\mathrm{C} = \frac{2\pi}{\hbar} C_\mathrm{A} v^2 \int_{-\infty}^{+\infty} D_+(E)\rho(E)f(E)\mathrm{d}E \qquad (5)$$

In order to solve Eq. 5, we assume the following approximations.

The temperature is room temperature or near room temperature. At room temperature, the following distribution function is assumed for $D_+(E)$ of electron acceptors in solution.

$$D_+(E) = \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{(E - E_0 - \lambda)^2}{4\lambda kT} \qquad (6)$$

Here E_0 is the energy at the redox potential of $\mathrm{A/A^{-\bullet}}$ and λ is the reorganization energy.

Equation 6 is used often by Gerischer's theory6) and also by Hopfield's theory.10)

$D_+(E)$ corresponds to the state density in solid state physics.10) When Eq. 6 is substituted into Eq. 5, we obtain

$$k_\mathrm{C} = \frac{2\pi}{\hbar} v^2 C_\mathrm{A} \int_{-\infty}^{+\infty} \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{(E - E_0 - \lambda)^2}{4\lambda kT} \rho(E)f(E)\mathrm{d}E \quad (7)$$

Equation 7 is the fundamental equation of cathodic electron transfer reactions at metal electrodes. We solve Eq. 7 under the following two cases.

A-1. Weak Coupling Case. We define the weak coupling case where the overlapping between the state density $D_+(E)$ and $\rho(E)f(E)$ is small. The situation is illustrated in Fig. 1.

In this case, the energy E of the electrons which contributes to Eq. 8 must be $E - E_\mathrm{f} \gg kT$. Under this condition Fermi distribution function is approximated by the following equation.

$$f(E) = \exp - \frac{E - E_\mathrm{f}}{kT} \qquad (8)$$

When Eq. 8 is used in Eq. 7, we get

$$k_\mathrm{C} = \frac{2\pi}{\hbar} v^2 C_\mathrm{A} \int_{-\infty}^{+\infty} \frac{\rho(E)}{\sqrt{4\pi\lambda kT}} \exp - \frac{(E - E_0 - \lambda)^2}{4\pi\lambda kT} \exp - \frac{E - E_\mathrm{f}}{kT} \mathrm{d}E \qquad (9)$$

Now we define E_1 and E_2 as follows.

$$-E_1 = -E_0 - \lambda \qquad (10)$$

$$-E_2 = -E_\mathrm{f} \qquad (11)$$

If we use Eqs. 10 and 11, Eq. 9 yields

$$k_\mathrm{C} = \frac{2\pi}{\hbar} v^2 C_\mathrm{A} \int_{-\infty}^{+\infty} \frac{\rho(E)}{\sqrt{4\pi\lambda kT}} \exp - \frac{(E - E_1)^2}{4\lambda kT} \exp - \frac{E - E_2}{kT} \mathrm{d}E \qquad (12)$$

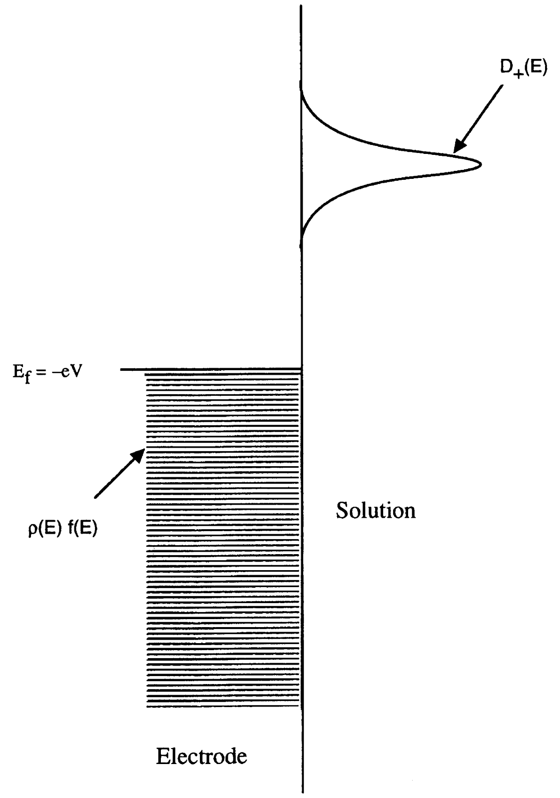

Fig. 1. A schematic illustration of weak coupling case for cathodic reaction at a metal electrode.

Equation 12 is rewritten as,

$$k_\mathrm{C} = \frac{2\pi}{\hbar} v^2 C_\mathrm{A} \int_{-\infty}^{+\infty} \frac{\rho(E)}{\sqrt{4\pi\lambda kT}} \exp - \left\{ \frac{(E - E_1)^2}{4\lambda kT} + \frac{E - E_2}{kT} \right\} \mathrm{d}E \qquad (13)$$

In Eq. 13, the following relation holds.

$$\left\{ \frac{(E - E_1)^2}{4\lambda kT} + \frac{E - E_2}{kT} \right\} = \frac{(E - E_1 + 2\lambda)^2}{4\lambda kT} + \frac{(E_1 - \lambda - E_2)}{kT} \qquad (14)$$

If we use Eq. 14, Eq. 13 yields

$$k_\mathrm{C} = \frac{2\pi}{\hbar} v^2 C_\mathrm{A} \int_{-\infty}^{+\infty} \frac{\rho(E)}{\sqrt{4\pi\lambda kT}} \exp - \frac{(E - E_1 + 2\lambda)^2}{4\lambda kT} \mathrm{d}E \times \exp - \frac{(E_1 - \lambda - E_2)}{kT} \qquad (15)$$

The state density $\rho(E)$ of metals changes monotonously depending on $\sqrt{E}$. The magnitude of the change of $\rho(E)$ is small within the overvoltage of 1 eV, as is shown later. Since the energy of electrons which contributes most to the integral is thought to be electrons excited thermally from the occupied states near E_f, as seen in Fig. 1.

Therefore, we can assume $\rho(E) = \rho(E_\mathrm{f})$ in Eq. 15 in order to solve Eq. 15.

Under the approximation of $\rho(E) = \rho(E_\mathrm{f})$, $\rho(E)$ can be taken outside the integration.

$$k_\mathrm{C} = \frac{2\pi}{\hbar} v^2 C_\mathrm{A} \frac{\rho(E_\mathrm{f})}{\sqrt{4\pi\lambda kT}} \int_{-\infty}^{+\infty} \exp - \frac{(E - E_1 + 2\lambda)^2}{4\lambda kT} \mathrm{d}E \times \exp - \frac{(E_1 - \lambda - E_2)}{kT} \qquad (16)$$

After integration is carried out, Eq. 16 gives

$$k_C = \frac{2\pi}{\hbar} v^2 C_A \rho(E_f) \exp - \frac{(E_1 - \lambda - E_2)}{kT} \tag{17}$$

A-2. Effect of Adsorption and Imposed Potential on $D_+(E)$. When an electrical potential is imposed on the working metal electrode, the Fermi level of the metal electrode shifts, since the Fermi level of the metal electrode is equal to electrochemical potential of the electrode, E_f is equal to the electrode potential. Therefore

$$E_f = -eV \tag{18}$$

Here V represents the electrode potential.

Imposed potential and the adsorption energy of A and A^- are expected to affect the distribution function $D_+(\varepsilon)$. We will discuss this problem according to Hopfield's model.[10)]

In order to obtain electron insertion spectrum we define the potential energy of $A+e_{vac}$, $E(A+e_{vac})$ and that of $A^{-\bullet}$, $E(A^{-\bullet})$ as follows

$$E(A + e_{vac}) = \frac{1}{2} k_0 x^2 \tag{19}$$

$$E(A^{-\bullet}) = \frac{1}{2} k_0 (x - x_a)^2 + \varepsilon_0 \tag{20}$$

Now we consider the virtual reduction process of $A + e_{vac} \rightarrow A^{-\bullet}$ in order to obtain $D_+(\varepsilon)$ in the absence of adsorption and imposed potential. Here e_{vac} represents an electron in the vacuum state.

From Eqs. 19 and 20,

$$\varepsilon = E(A^{-\bullet}) - E(A + e_{vac}) = -k_0 x_a x + \frac{1}{2} k_0 x_a^2 + \varepsilon_0 \tag{21}$$

From Eq. 21, we obtain

$$x = \frac{-\varepsilon + \varepsilon_0 + \lambda}{k_0 x_a} \tag{22}$$

Here λ is reorganization energy defined as $\frac{1}{2} k_0 x_a^2 = \lambda$

Now we assume a Boltzmann distribution for $E(A+e_{vac})$.

$$D_+(\varepsilon) = \exp - \frac{E(A + e_{vac})}{kT} = \exp - \frac{k_0 x^2}{2kT} \tag{23}$$

From Eqs. 22 and 23 we get

$$D_+(\varepsilon) = \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{(\varepsilon - \varepsilon_0 - \lambda)^2}{4\lambda kT} \tag{24}$$

where $\frac{1}{\sqrt{4\pi\lambda kT}}$ in Eq. 24 is the normalization factor of $D_+(\varepsilon)$.

Equation 24 has the same form as Eq. 6. ε_0 represents the redox potential of $A/A^{-\bullet}$ in the absence of adsorption on the electrode. Now let's consider the effect of adsorption on the electrode surface and the imposed potential.

When reactant A interacts with the electrode surface and feels the imposed electric field, Eq. 19 can be expressed as

$$E(A + e_{vac}) = \frac{1}{2} k_0 x^2 - \Delta\varepsilon_{int,i} - e\alpha_i \eta \tag{25}$$

Here the suffix i represents the initial state. $-\Delta\varepsilon_{int,i}$ represent the interaction energy of A with the electrode surface before the electron transfer and η represents overvoltage defined as,

$$\eta = V - V_{eq} \tag{26}$$

$$V_{eq} = V_0 + \frac{kT}{e} \ln \frac{C_{Ox}}{C_R} \tag{27}$$

Here V_{eq} and V_0 represents the equilibrium potential and the redox potential of A/A^- system, respectively. C_{Ox} and C_R represents the concentration of the oxidized and reduced species, respectively. Equation 27 is identical with the equilibrium potential in the classical electrochemistry.

In Eq. 25, parameter α_i represents the shielding factor of the overvoltage by the solvent layer between the electrode surface and A. The imposed overvolutage is thought to be shielded by such a solvent layer. Under this approximation, the electron in A molecule is assumed to feel a shielded electric field $\alpha_i \eta$. Parameter α_i corresponds to the transfer coefficients in the classical theory of electrochemistry, i.e. the Butler–Volmer equation of electrode reaction, although the physical meaning is different in the present case.

Similarly taking the effect of adsorption and imposed potential into consideration for $A^{-\bullet}$, we can write Eq. 20 as

$$E(A_{ad}^{-\bullet}) = \frac{1}{2} k_0 (x - x_a)^2 + \varepsilon_0 - \Delta\varepsilon_{int,f} - e\alpha_f \eta \tag{28}$$

Here $-\Delta\varepsilon_{int,f}$ represents the interaction energy of $A^{-\bullet}$ with the electrode surface at the same instant with the electron transfer. The suffix f represents the final state. The interaction energy $\Delta\varepsilon_{int,f}$ plays an important role in hydrogen evolution reaction as is seen later. It is a new concept characteristic to quantum mechanical electron transfer theory at the surface of metal electrodes. Hereafter we call this "Electron transfer adsorption energy".

From Eqs. 25 and 28, we obtain

$$\varepsilon = E(A^{-\bullet}) - E(A + e_{vac}) = -k_0 x_a x + \varepsilon_0 - \Delta\varepsilon_{fi} - e\alpha_{fi} \eta + \lambda \tag{29}$$

where,

$$\Delta\varepsilon_{fi} = \Delta\varepsilon_{int,f} - \Delta\varepsilon_{int,i} \tag{30}$$

$$\alpha_{fi} = \alpha_f - \alpha_i \tag{31}$$

From Eq. 29

$$x = \frac{-\varepsilon + \varepsilon_0 - \Delta\varepsilon_{fi} - e\alpha_{fi} \eta + \lambda}{k_0 x_a} \tag{32}$$

We obtain from Eqs. 23 and 32

$$\begin{aligned} D_+(\varepsilon) &= \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{k_0 x^2}{2kT} \\ &= \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{(\varepsilon - \varepsilon_0 + \Delta\varepsilon_{fi} + e\alpha_{fi} \eta - \lambda)^2}{4\lambda kT} \end{aligned} \tag{33}$$

If we assume

$$E_0 = \varepsilon_0 - \Delta\varepsilon_{fi} - e\alpha_{fi} \eta \tag{34}$$

Equation 32 becomes identical with Eq. 6. Moreover, Eq. 33 is reduced to Eq. 24 for $\Delta\varepsilon_{fi} = \eta = 0$. Therefore Eq. 33 is the genaral expression for the electron insertion spectrum $D_+(\varepsilon)$ irrespective of the presence or absence of adsorption and imposed potential.

Quantum Mechanical Butler–Volmer Equation. Equations 10, 11, 18, and 34 yield

$$E_1-\lambda-E_2=E_0+\mathrm{e}V=\varepsilon_0-\Delta\varepsilon_{\mathrm{fi}}+\mathrm{e}(1-\alpha_{\mathrm{fi}})\eta+\mathrm{e}V_{\mathrm{eq}} \tag{35}$$

Equations 17 and 35 give

$$k_{\mathrm{C}}=\frac{2\pi}{\hbar}v^2C_{\mathrm{A}}\rho(E_{\mathrm{f}})\exp-\frac{\varepsilon_0-\Delta\varepsilon_{\mathrm{fi}}+\mathrm{e}(1-\alpha_{\mathrm{fi}})\eta+\mathrm{e}V_{\mathrm{eq}}}{kT} \tag{36}$$

The cathodic current i_{C} is

$$i_{\mathrm{C}}=i_0^{\mathrm{c}}\exp-\frac{\mathrm{e}(1-\alpha_{\mathrm{fi}})\eta}{kT} \tag{37}$$

Here,

$$i_0^{\mathrm{c}}=\mathrm{e}k_{\mathrm{C}}^0=\frac{2\pi\mathrm{e}}{\hbar}v^2C_{\mathrm{A}}\rho(E_{\mathrm{f}})\exp-\frac{\varepsilon_0-\Delta\varepsilon_{\mathrm{fi}}+\mathrm{e}V_{\mathrm{eq}}}{kT} \tag{38}$$

Equation 37 resembles the Butler–Volmer equation in classical electrochemistry. Since i_0^{c} is the current at η=0, Eq. 38 expresses the exchange current.

Equation 37 is in the same form as the classical Butler–Volmer equation which is used successfully to explain the potential dependence of cathodic (or anodic) current.[1,17] Consequently, it gives a quantum mechanical expression of the Butler–Volmer equation. $1-\alpha_{\mathrm{fi}}$ in Eq. 37 corresponds to transfer coefficient in the classical theory, although it has a different physical meaning in the present case as was already discussed.

A-3. Strong Coupling. We define a strong coupling case where the overlapping between the electron insertion spectrum $D_+(E)$ and the state density of the occupied states of the metal electrode $\rho(E)f(E)$ is good. In this case $E \gg kT$ is not a good approximation. Therefore we cannot apply a Bolzmann approximation for $f(E)$. We have to treat the problem differently from the weak coupling case. The situation of the strong coupling case for cathodic electron transfer is illustrated in Fig. 2.

We solve the fundamental equation of Eq. 7 as follows.

In Eq. 7, we assume $\rho(E)=\rho(E_{\mathrm{f}})$, because the energy of electrons which contribute most to the integral is thought to be near E_{f}, as is seen in Fig. 2. Under this approximation, Eq. 7 is written as

$$k_{\mathrm{C}}=\frac{2\pi}{\hbar}v^2C_{\mathrm{A}}\frac{\rho(E_{\mathrm{f}})}{\sqrt{4\pi\lambda kT}}\int_{-\infty}^{+\infty}\exp-\frac{(E-E_0-\lambda)^2}{4\lambda kT}f(E)\mathrm{d}E \tag{39}$$

Equation 39 is rewritten as

$$k_{\mathrm{C}}=\frac{2\pi}{\hbar}v^2C_{\mathrm{A}}\frac{\rho(E_{\mathrm{f}})}{\sqrt{4\pi\lambda kT}}\int_{-\infty}^{+\infty}\exp\left\{-\frac{(E-E_0-\lambda)^2}{4\lambda kT}+\ln f(E)\right\}\mathrm{d}E \tag{40}$$

Now we define

$$F(E)=-\frac{(E-E_0-\lambda)^2}{4\lambda kT}+\ln f(E) \tag{41}$$

Then Eq. 40 can be written as,

$$k_{\mathrm{C}}=\frac{2\pi}{\hbar}v^2C_{\mathrm{A}}\frac{\rho(E_{\mathrm{f}})}{\sqrt{4\pi\lambda kT}}\int_{-\infty}^{+\infty}\exp F(E)\mathrm{d}E \tag{42}$$

Equation 41 can be solved by Laplace's method.[4]

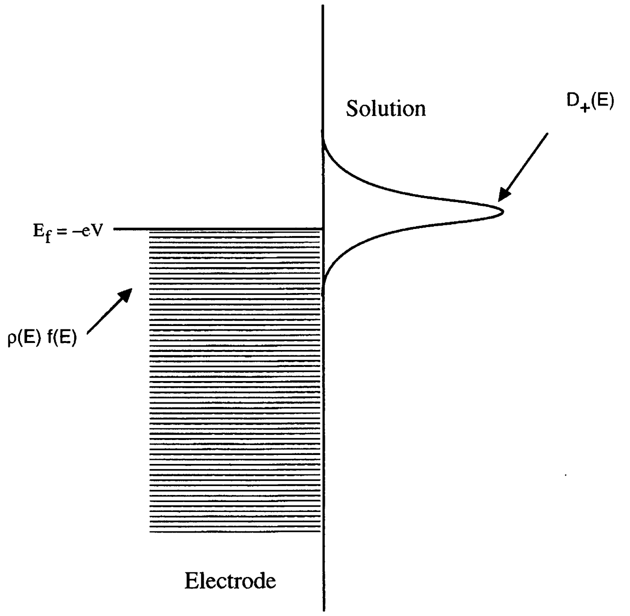

Fig. 2. A schematic illustration of strong coupling case for cathodic reaction at a metal electrode.

The cathodic electron transfer rate obtained by this method is

$$k_{\mathrm{C}}=\frac{2\pi}{\hbar}v^2C_{\mathrm{A}}\sqrt{\frac{kT}{2\lambda}}\rho(E_{\mathrm{f}})\exp-\frac{(E^*-E_0-\lambda)^2}{4\lambda kT} \tag{43}$$

Here E^* satisfies the following equation.

$$\frac{(E^*-E_0-\lambda)}{2\lambda}=\frac{1}{1+\exp\frac{E^*-E_{\mathrm{f}}}{kT}} \tag{44}$$

In the presence of adsorption and imposed potential substitution of Eq. 34 into E_0 of Eq. 43 gives

$$k_{\mathrm{C}}=\frac{2\pi}{\hbar}v^2C_{\mathrm{A}}\sqrt{\frac{kT}{2\lambda}}\rho(E_{\mathrm{f}})\exp-\frac{(E^*-\varepsilon_0+\Delta\varepsilon_{\mathrm{fi}}+\mathrm{e}\alpha_{\mathrm{fi}}\eta-\lambda)^2}{4\lambda kT} \tag{45}$$

From Eq. 45 the current-potential relation in the strong coupling case is obtained as follows.

$$i_{\mathrm{C}}=\frac{2\pi\mathrm{e}}{\hbar}v^2C_{\mathrm{A}}\sqrt{\frac{kT}{2\lambda}}\rho(E_{\mathrm{f}})\exp-\frac{(E^*-\varepsilon_0+\Delta\varepsilon_{\mathrm{fi}}+\mathrm{e}\alpha_{\mathrm{fi}}\eta-\lambda)^2}{4\lambda kT} \tag{46}$$

B) Anodic Process. Now let's consider the following anodic reaction at the metal electrode.

$$\mathrm{D}\rightarrow\mathrm{D}^++\mathrm{e}_{\mathrm{el}} \tag{47}$$

Here D represents an electron donor near the electrode.

For the above anodic electron transfer from the electron donor D to a vacant state of the matal electrode, the electron transfer reta k_{A} is expressed by the following equation[9] similar to Eq. 2.

$$k_{\mathrm{A}}=\frac{2\pi}{\hbar}C_{\mathrm{D}}v^2\int_{-\infty}^{+\infty}D_+(E)D_-(E)\mathrm{d}E \tag{48}$$

Here, $D_+(E)$ in Eq. 48 is the state density of holes at the metal electrode. It can be expressed as[4]

$$D_+(E)=\rho(E)\{1-f(E)\} \tag{49}$$

Then, Eq. 48 can be written as,

$$k_A = \frac{2\pi}{\hbar} C_D v^2 \int_{-\infty}^{+\infty} \rho(E)\{1 - f(E)\} D_-(E) \mathrm{d}E \tag{50}$$

where $D_-(E)$: Distribution function of electrons in electron donors, i.e. reduced species D in solution. It is also called electron removal spectrum.[10)]

$\rho(E)$: State density of the metal electrode.

$f(E)$: Fermi–Dirac distribution function.

$\rho(E)(1-f(E))$: Distribution function of holes at the metal electrode.

v: Electron exchange integral between an electron donor D and a hole at the metal electrode.

Equation 50 can be solved under the following approximations.

For the distribution function $D_-(E)$ of the electron donor D the following expression is used.[6,10)]

$$D_-(E) = \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{(E - E_0 + \lambda)^2}{4\lambda kT} \tag{51}$$

Here E_0 represents the energy level of the electron donor which corresponds to the redox potential of the D^+/D redox couple. λ is the reoganization energy.[6,10)]

Substitution of Eq. 51 into Eq. 50 gives

$$k_A = \frac{2\pi}{\hbar} v^2 C_D \int_{-\infty}^{+\infty} \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{(E - E_0 + \lambda)^2}{4\lambda kT} \rho(E)\{1 - f(E)\} \mathrm{d}E \tag{52}$$

Equation 52 is the fundamental equation of anodic electron transfer rate at metal electrodes.

B-1. Weak Coupling Case. We define the weak coupling case where the overlapping between the state density $D_-(E)$ of electron donor D and that of holes at metal electrode $\rho(E)(1-f(E))$ is poor. The situation of weak coupling case is illlustrated in Fig. 3.

In this case $E_f - E \gg kT$ must be a good approximation. Under this condition,

$$1 - f(E) = \exp - \frac{E_f - E}{kT} \tag{53}$$

When Eq. 53 is substituted into Eq. 52,

$$k_A = \frac{2\pi}{\hbar} \cdot \frac{C_D}{\sqrt{4\pi\lambda kT}} v^2 \int_{-\infty}^{+\infty} \rho(E) \exp - \frac{E_f - E}{kT} \cdot \exp - \frac{(E - E_0 + \lambda)^2}{4\lambda kT} \mathrm{d}E \tag{54}$$

is obtained. Now we assume that the $\rho(E)$ value that contributes the most to the integral is $\rho(E_f)$, i.e. the density of the metal near the Fermi level. Then $\rho(E)$ can be taken outside the integral.

$$k_A = \frac{2\pi}{\hbar} \cdot \frac{C_D v^2 \rho(E_f)}{\sqrt{4\pi\lambda kT}} \int_{-\infty}^{+\infty} \exp - \frac{E_f - E}{kT} \cdot \exp - \frac{(E - E_0 + \lambda)^2}{4\lambda kT} \mathrm{d}E \tag{55}$$

Now we define

$$-E_1 = -E_0 + \lambda \tag{56}$$

$$-E_2 = -E_f \tag{57}$$

Equations 55, 56, and 57 yield

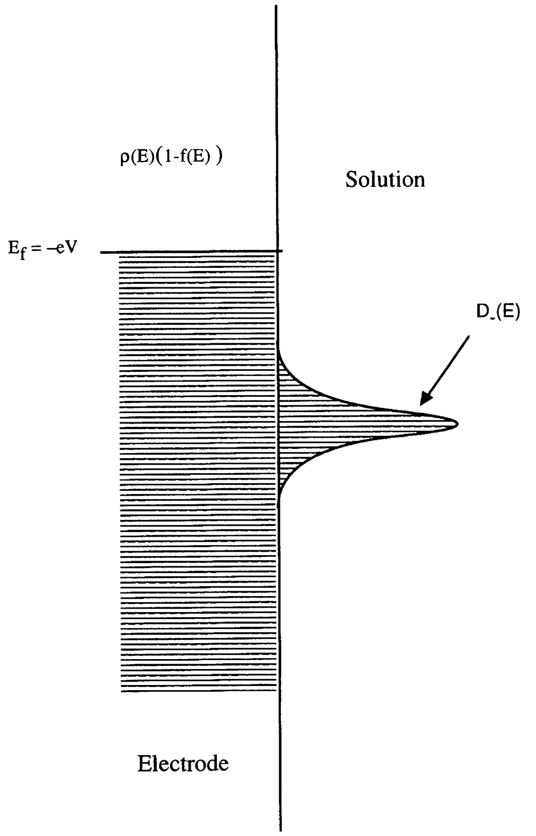

Fig. 3. A schematic illustration of weak coupling case for anodic reaction at a metal electrode.

$$k_A = \frac{2\pi}{\hbar} \cdot \frac{C_D v^2 \rho(E_f)}{\sqrt{4\pi\lambda kT}} \int_{-\infty}^{+\infty} \exp - \left\{ \frac{(E - E_1)^2}{4\lambda kT} - \frac{E - E_2}{kT} \right\} \mathrm{d}E \tag{58}$$

In Eq. 58 the following relation holds.

$$\left\{ \frac{(E - E_1)^2}{4\lambda kT} - \frac{E - E_2}{kT} \right\} = \frac{(E - E_1 - 2\lambda)^2}{4\lambda kT} + \frac{(E_2 - E_1 - \lambda)}{kT} \tag{59}$$

When this relation is used, Eq. 58 becomes

$$k_A = \frac{2\pi}{\hbar} \cdot \frac{C_D v^2 \rho(E_f)}{\sqrt{4\pi\lambda kT}} \int_{-\infty}^{+\infty} \exp - \frac{(E - E_1 - 2\lambda)^2}{4\lambda kT} \mathrm{d}E \times \exp - \frac{(E_2 - E_1 - \lambda)}{kT} \tag{60}$$

After the integral of Eq. 60 is carried out, we get

$$k_A = \frac{2\pi}{\hbar} C_D v^2 \rho(E_f) \exp - \frac{(E_2 - E_1 - \lambda)}{kT} \tag{61}$$

B-2. Effect of Adsorption and Imposed Potential on $D_-(E)$. Imposed potential and the adsorption energy of D and D^+ on the electrode surface are expected to affect the electron removal spectrum $D_-(\varepsilon)$. We will discuss this problem according to Hopfield's model.[10)]

In order to obtain electron removal spectrum we define the potential energy of D, $E(\mathrm{D})$ and $D^{+\bullet} + e_{\mathrm{vac}}$, $E(\mathrm{D}^{+\bullet} + e_{\mathrm{vac}})$ as follows.

$$E(\mathrm{D}) = \frac{1}{2} k_0 (x - x_a)^2 + \varepsilon_0 \tag{62}$$

$$E(\mathrm{D}^{+\bullet} + e_{\mathrm{vac}}) = \frac{1}{2} k_0 x^2 \tag{63}$$

From Eqs. 62 and 63 we have

$$\varepsilon = E(\mathrm{D}) - E(\mathrm{D}^{+\bullet} + \mathrm{e}_{\mathrm{vac}}) = -k_0 x_{\mathrm{a}} x + \frac{1}{2} k_0 x_{\mathrm{a}}^2 + \varepsilon_0 \tag{64}$$

Equation 64 gives

$$x = \frac{-\varepsilon + \varepsilon_0 + \lambda}{k_0 x_{\mathrm{a}}} \tag{65}$$

where λ is reorganization energy defined as $\frac{1}{2}k_0 x_{\mathrm{a}}^2 = \lambda$. Equation 65 gives

$$x - x_{\mathrm{a}} = \frac{-\varepsilon + \varepsilon_0 - \lambda}{k_0 x_{\mathrm{a}}} \tag{66}$$

Now we assume a Boltzmann distribution for $E(\mathrm{D})$.

$$D_-(\varepsilon) = \exp - \frac{E(\mathrm{D})}{kT} = \exp - \frac{\frac{1}{2}k_0 (x - x_{\mathrm{a}})^2 + \varepsilon_0}{kT}$$
$$= \exp - \frac{\frac{1}{2}k_0 (x - x_{\mathrm{a}})^2}{kT} \tag{67}$$

where the constant ε_0 was neglected in Eq. 67, since the energy level of electron is thought to be located at ε_0 at the initial state without thermal excitation.

Substitution of Eq. 65 into Eq. 66 gives

$$D_-(\varepsilon) = \exp - \frac{k_0}{2kT} \cdot \frac{(-\varepsilon + \varepsilon_0 - \lambda)^2}{(k_0 x_{\mathrm{a}})^2} = \exp - \frac{(-\varepsilon + \varepsilon_0 - \lambda)^2}{4\lambda kT} \tag{68}$$

When Eq. 68 is normalized,

$$D_-(\varepsilon) = \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{(-\varepsilon + \varepsilon_0 - \lambda)^2}{4\lambda kT} \tag{69}$$

Equation 69 has the same form as Eq. 51. ε_0 represents the redox potential of $\mathrm{D}^{+\bullet}/\mathrm{D}$ in the absence of adsorption on the electrode surface.

Now let's consider the effect of adsorption on electrode surface and imposed potential on the electron removal spectrum of Eq. 69.

When an oxidized species $\mathrm{D}^{+\bullet}$ interacts with the electrode surface and feels the imposed electric field, Equation 62 is expressed as,

$$E(\mathrm{D}^{+\bullet} + \mathrm{e}_{\mathrm{vac}}) = \frac{1}{2} k_0 x^2 - \Delta\varepsilon_{\mathrm{int,f}} + \alpha_{\mathrm{f}} \mathrm{e} \eta \tag{70}$$

Here $-\Delta\varepsilon_{\mathrm{int,f}}$ represent the interaction energy (adsorption energy) of $\mathrm{D}^{+\bullet}$ with the electrode surface at the same instant with the electron transfer and parameter α_{f} represents the shielding facter of overvoltage η by the solvent layer between the electrode, surface and $\mathrm{D}^{+\bullet}$. $-\Delta\varepsilon_{\mathrm{int,f}}$ represents the anodic "electron transfer adsorption energy" of $\mathrm{D}^{+\bullet}$ on the electrode surface.

Similarly taking the effect of adsorption and imposed potential into consideration for the reactant D, Eq. 62 can be written as,

$$E(\mathrm{D}) = \frac{1}{2} k_0 (x - x_{\mathrm{a}})^2 + \varepsilon_0 - \Delta\varepsilon_{\mathrm{int,i}} - \alpha_{\mathrm{i}} \mathrm{e} \eta \tag{71}$$

Here $-\Delta\varepsilon_{\mathrm{int,i}}$ is the adsorption energy of D before electron transfer. The suffix i represents the initial state.

Equations 70 and 71 yield

$$\varepsilon = E(\mathrm{D}) - E(\mathrm{D}^{+\bullet} + \mathrm{e}_{\mathrm{vac}})$$
$$= -k_0 x_{\mathrm{a}} x + \frac{1}{2} k_0 x_{\mathrm{a}}^2 + \varepsilon_0 - \Delta\varepsilon_{\mathrm{int,fi}} - \alpha_{\mathrm{fi}} \mathrm{e} \eta \tag{72}$$

Here

$$\Delta\varepsilon_{\mathrm{fi}} = \Delta\varepsilon_{\mathrm{int,f}} - \Delta\varepsilon_{\mathrm{int,i}} \tag{73}$$

$$\alpha_{\mathrm{fi}} = \alpha_{\mathrm{f}} + \alpha_{\mathrm{i}} \tag{74}$$

are defined. From Eq. 72

$$x - x_{\mathrm{a}} = \frac{-(\varepsilon - \varepsilon_0 + \lambda - \Delta\varepsilon_{\mathrm{int,fi}} + \alpha_{\mathrm{fi}} \mathrm{e} \eta)}{k_0 x_{\mathrm{a}}} \tag{75}$$

Equations 75 and 67 yield

$$D_-(\varepsilon) = \frac{1}{\sqrt{4\pi\lambda kT}} \exp - \frac{\{\varepsilon - (\varepsilon_0 + \Delta\varepsilon_{\mathrm{int,fi}} - \alpha_{\mathrm{fi}} \mathrm{e} \eta) + \lambda\}^2}{4\lambda kT} \tag{76}$$

If we assume

$$E_0 = \varepsilon_0 + \Delta\varepsilon_{\mathrm{fi}} - \mathrm{e}\alpha_{\mathrm{fi}} \eta \tag{77}$$

Equation 76 becomes equal to Eq. 51. Moreover, Eq. 76 is reduced to Eq. 68 for $\Delta\varepsilon_{\mathrm{fi}} = \eta = 0$. Therefore Eq. 76 is the general expression for electron removal spectrum $D_-(\varepsilon)$ which expresses the effect of adsorption and imposed potential.

Quantum Mechanical Butler–Volmer Equation. Equations 18, 26, 56, 57, and 77 give

$$-(E_2 - E_1 - \lambda) = -(E_{\mathrm{f}} - E_0) = \varepsilon_0 + \Delta\varepsilon_{\mathrm{fi}} + \mathrm{e}(1 - \alpha_{\mathrm{fi}})\eta + \mathrm{e}V_{\mathrm{eq}} \tag{78}$$

Substitution of Eq. 78 into Eq. 61 gives

$$k_{\mathrm{A}} = \frac{2\pi}{\hbar} C_{\mathrm{D}} v^2 \rho(E_{\mathrm{f}}) \exp \frac{\varepsilon_0 + \Delta\varepsilon_{\mathrm{fi}} + \mathrm{e}(1 - \alpha_{\mathrm{fi}})\eta + \mathrm{e}V_{\mathrm{eq}}}{kT} \tag{79}$$

The anodic current i_{A} is

$$i_{\mathrm{A}} = i_0^{\mathrm{a}} \exp \frac{\mathrm{e}(1 - \alpha_{\mathrm{fi}})\eta}{kT} \tag{80}$$

Here

$$i_0^{\mathrm{a}} = \frac{2\pi \mathrm{e}}{\hbar} C_{\mathrm{D}} v^2 \rho(E_{\mathrm{f}}) \exp \frac{\varepsilon_0 + \Delta\varepsilon_{\mathrm{fi}} + \mathrm{e}V_{\mathrm{eq}}}{kT} \tag{81}$$

Equation 80 has a reasonable from, since i_{A} increases with increasing η. Equation 80 resembles Butler–Volmer equation in classical electrochemistry.

Since i_0^{a} is the current at $\eta = 0$, Eq. 81 expresses the exchange current.

Thus Eqs. 80 and 81 form the quantum mechanical expression of Butler–Volmer equation and the exchange current, respectively, for the anodic reaction in the case of weak coupling.

B-3. Strong Coupling. We define a strong coupling case where the overlapping between the electron removal spectrum $D_-(E)$ and state density of the unoccupied states of the metal electrode $\rho(E)(1 - f(E))$ is good. In this case $E_{\mathrm{f}} - E \gg kT$ is not a good approximation. Therefore we cannot apply the Boltzmann approximation for $f(E)$. We have to treat the problem differently from the weak coupling case. The situation of the strong coupling case for anodic electron transfer is illustrated in Fig. 4.

In Eq. 52 the $\rho(E)$ value that contributes the most to the integral is reasonably assumed to be $\rho(E_{\mathrm{f}})$ as is seen in Fig. 4.

Under this approximation, $\rho(E)$ can be taken outside the integral. Furthermore we define

$$g(E) = 1 - f(E) = \frac{1}{1 + \exp - \frac{E - E_f}{kT}} \tag{82}$$

Then Eq. 52 is written as

$$k_A = \frac{2\pi}{\hbar} v^2 C_D \frac{\rho(E_f)}{\sqrt{4\pi\lambda kT}} \int_{-\infty}^{+\infty} \exp - \frac{(E - E_0 + \lambda)^2}{4\lambda kT} g(E) \mathrm{d}E \tag{83}$$

Equation 83 is rewritten as

$$k_A = \frac{2\pi}{\hbar} v^2 C_D \frac{\rho(E_f)}{\sqrt{4\pi\lambda kT}} \int_{-\infty}^{+\infty} \exp \left\{ - \frac{(E - E_0 + \lambda)^2}{4\lambda kT} + \ln g(E) \right\} \mathrm{d}E \tag{84}$$

Here we define

$$G(E) = - \frac{(E - E_0 - \lambda)^2}{4\lambda kT} + \ln g(E) \tag{85}$$

Then Eq. 84 becomes

$$k_A = \frac{2\pi}{\hbar} v^2 C_D \frac{\rho(E_f)}{\sqrt{4\pi\lambda kT}} \int_{-\infty}^{+\infty} \exp G(E) \mathrm{d}E \tag{86}$$

Equation 86 can be solved by Laplace's method.[4)]

The anodic reaction rate obtained by this method is

$$k_A = \frac{2\pi}{\hbar} v^2 C_D \sqrt{\frac{kT}{2\lambda}} \rho(E_f) \exp - \frac{(E^* - E_0 - \lambda)^2}{4\lambda kT} \tag{87}$$

Here E^* is determined by Eq. 44.

In the presence of adsorption and imposed potential, the relation of Eq. 77 should be substituted into Eq. 87. Then we get the following current potential relation for the anodic electron transfer rate in the strong coupling case.

$$k_A = \frac{2\pi}{\hbar} v^2 C_D \sqrt{\frac{kT}{2\lambda}} \rho(E_f) \exp - \frac{(E^* - \varepsilon_0 - \Delta\varepsilon_{fi} + e\alpha_{fi}\eta - \lambda)^2}{4\lambda kT} \tag{88}$$

Because of $i_A = ek_A$, the current potential relation of anodic electron transfer in the strong coupling case is obtained from Eq. 88 as

$$i_A = \frac{2\pi e}{\hbar} v^2 C_D \sqrt{\frac{kT}{2\lambda}} \rho(E_f) \exp - \frac{(E^* - \varepsilon_0 - \Delta\varepsilon_{fi} + e\alpha_{fi}\eta - \lambda)^2}{4\lambda kT} \tag{89}$$

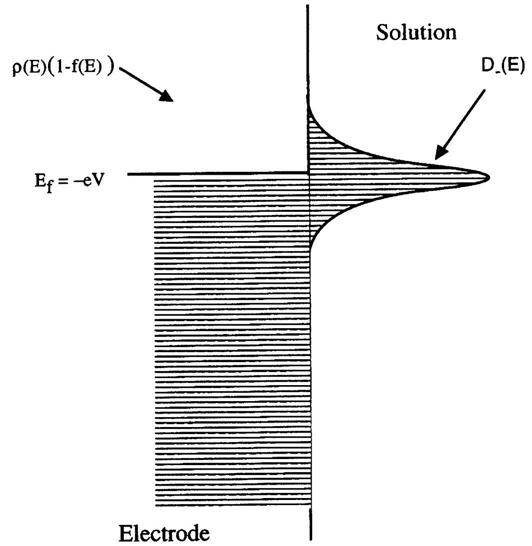

Fig. 4. A schematic illustration of strong coupling case for anodic reaction at a metal electrode.

Results and Discussion

A) Comparison of the Present Theory with the Classical Theory of Electrode Reaction. Since the electron transfer rate at metal electrodes based on quantum theory is in a Gaussian form,[4)] it does not explain well the experimental results of electrode reactions.[8)] The weak coupling case shown in Figs. 1 and 3 corresponds to the case of very large overpotential which is larger than the width of the distribution function of an electron acceptor or electron donor. The electrode reaction rates obtained in the weak coupling cases of the present theory are exponential. They correspond well to the classical Butler–Volmer equation. Since the Butler–Volmer equation is applied well to electrochemistry,[1)] the above difficulty is solved in the weak coupling case of the present theory. On the other hand in the strong coupling case which corresponds to the small overpotential, the Gaussian current–potential relationship is obtained. In this case, the experimental data of the exponential relationship as plotted by Khan and Bockris is only partly explained. Gaussian type potential dependence in the strong coupling case agrees with the result by Levich.[4)]

The classical theory is based on the transition state theory that assumes an activated complex as an intermediate of the electron transfer at the electrode surface.[1)] However, the present theory does not assume such an activated complex nor an intermediate. It describes the electron transfer rate at the metal electrode quantum mechanically based on the direct interaction between the electrode and molecules near the electrode.

The parameter α introduced in Eq. 25 corresponds to the transfer coefficient of the classical theory. Transfer coefficient of the classical theory reflects symmetry of the potential curves at the transition state.[1)] However, α in the present theory represents a shielding factor of the overvoltage, η. Although the properties of metal electrodes are not included in the classical theory, the state density of metal electrode $\rho(E_f)$ is included in the present theory. Moreover the property of metal electrode is reflected indirectly in the interaction energy $\Delta\varepsilon_{fi}$ and v.

Besides these characteristic features, the present theory has the following advantages over the classical theory.[1)]

The rate of the electrode reaction is expressed in the classical theory as

$$k_C = k_C^0 \exp - \frac{\alpha F \eta}{RT}$$

where F and α represent Faraday constant and transfer coefficient, respectively.

The reaction rate k_C^0 is a mere parameter and can not be evaluated quantitatively in the calssical theory. However, the present theory can evaluate the magnitude of k_C^0 in the case of weak coupling.

For instance, the standard rate constant k_C^0 for cathodic reaction is from Eq. 38

$$k_C^0 = \frac{2\pi}{\hbar} v^2 C_A \rho(E_f) \exp - \frac{\varepsilon_0 - \Delta\varepsilon_{fi} + eV_{eq}}{kT} \tag{38a}$$

The exchange current is written as

$$i_0^c = ek_C^0 = \frac{2\pi e}{\hbar} v^2 C_A \rho(E_f) \exp - \frac{\varepsilon_0 - \Delta\varepsilon_{fi} + eV_{eq}}{kT} \tag{38b}$$

The exchange current plays an important role in the present theory.

Here let's consider the physical meaning of exchange current expressed by Eq. 38. Figure 5 shows the meaning schematically. The electrode potential is located at the equilibrium potential V_{eq} and the center of the distribution function $D_+(E)$ is located at $\varepsilon_0 - \Delta\varepsilon_{fi}$ as shown in Fig. 5. Electrons at electrode surface interact with electron acceptor molecules with the exchange integral v. The activation energy is $\Delta E = \varepsilon_0 - \Delta\varepsilon_{fi} + eV_{eq}$. Then thermally excited electrons are transferred from the metal electrode to the electron acceptor molecules at the electrode surface.

The exchange current is the current that flows accompanied with this electron transfer interaction as is illustrated in Fig. 5.

For an anodic reaction, Eq. 81 is

$$i_0^a = \frac{2\pi e}{\hbar} C_D v^2 \rho(E_f) \exp \frac{\varepsilon_0 + \Delta\varepsilon_{fi} + eV_{eq}}{kT} \tag{81b}$$

and

$$k_A^0 = \frac{2\pi}{\hbar} C_D v^2 \rho(E_f) \exp \frac{\varepsilon_0 + \Delta\varepsilon_{fi} + eV_{eq}}{kT} \tag{81a}$$

These equations have clear expressions as well as the physical meanings and they can be evaluated quantitatively.

Now let's consider the equilibrium condition.

At equilibrium Eqs. 37 and 80 yield

$$i_0^c \exp - \frac{e(1-\alpha)\eta}{kT} = i_0^a \exp \frac{e(1-\alpha)\eta}{kT} \tag{D1}$$

Here the suffix of α was omitted for simplicity. Equation D1 gives

$$\eta = \frac{kT}{2e(1-\alpha)} \ln \frac{i_0^c}{i_0^a} \tag{D2}$$

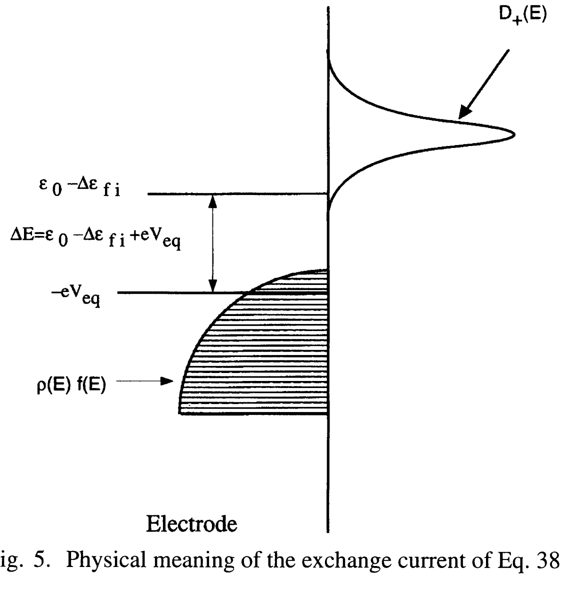

Fig. 5. Physical meaning of the exchange current of Eq. 38.

If $i_0^c = i_0^a$ is asuumed, Eq. D2 yields $\eta = 0$.

Equations 26 and 27 and the condition of $\eta = 0$ yield

$$V = V_{eq} = V_0 + \frac{kT}{e} \ln \frac{C_{Ox}}{C_R} \tag{D3}$$

Equation D3 represents the Nernst Equation. This result agrees well with the classical theory.

In the case of $i_0^c = i_0^a = i_0$, we obtain the following current–overpotential relation.

$$i = -i_C + i_A = i_0 \left[-\exp - \frac{e(1-\alpha)\eta}{kT} + \exp \frac{e(1-\alpha)\eta}{kT} \right] \tag{D4}$$

Equation D4 is in the same form as the classical Butler–Volmer equation. In Eq. D4 the first term describes the cathodic component current and the second gives the anodic contribution.

Generally speaking i_0^c is not equal to i_0^a. This means that the classical Nernst and Butler–Volmer equations are specific cases in the present theory. It should be noted that Eq. 37 is also in the same form as Tafel equation with the typical Tafel slope of 0.118V for $\alpha = 0.5$. These results show that the weak coupling case of the present theory corresponds well to the theory of classical electrochemistry. In the present theory redox species of strong coupling cases in cathodic and anodic electron transfer correspond to strong oxidants and strong reductants, respectively. Redox species of weak coupling cases in cathodic and anodic electron transfer correspond to weak oxidants and weak reductants, respectively. It is apparent that the number of weak oxidants and weak reductants used for electrochemical experiments is larger than that of strong oxidants and strong reductants. This fact seems to answer the question posed by Bockris et al.[8)] why the Butler–Volmer (exponential) equation can be applied successfully to a large number of electrochemical reactions.

B) Application to Hydrogen Evolution Reaction. As for the rate determining step of hydrogen evolution reaction, the following two mechanisms are considered.[16,17)]

a) Electron transfer of Eq. D5 is the rate determining step.

$$H^+ + e \rightarrow \cdot H_{ad} \tag{D5}$$

b) Recombination reaction of Eq. D6 is the rate determining step.

$$\cdot H_{ad} + \cdot H_{ad} \rightarrow H_2 \tag{D6}$$

Here $\cdot H_{ad}$ represents one hydrogen adsorbed on the electrode surface.

c) Besides Eqs. D5 and D6, an electrochemical mechanism is proposed, where following reaction is the rate determining step.[15,17)]

$$\cdot H_2^+ + e \rightarrow H_2 \tag{D7}$$

For hydrogen evolution reaction, $\varepsilon_0 = -2.1$ eV,[14)] and $-eV_0 = -4.5$[16,17)] from the vacuum level are reported. Consequently $\varepsilon_0 - (-eV_0) = 2.4 \text{ eV} \gg kT$. This condition corresponds well to the weak coupling case. Therefore Eq. 38 can be used for this reaction. Now we will discuss this problem based on the present theory in the weak coupling case.

Now let's consider $\Delta\varepsilon_{\rm fi}$ for the cathodic reaction of Eq. D5. From Eq. 30

$$\Delta\varepsilon_{\rm fi} = \Delta\varepsilon_{\rm int,f} - \Delta\varepsilon_{\rm int,i} \tag{30}$$

For the reaction of Eq. D5 cathodic "electron transfer adsorption energy" $\Delta\varepsilon_{\rm int,f}$ represents the adsorption energy of atomic hydrogen $\cdot$H on the electrode surface which is formed at the same instant with the cathodic electron transfer. $\Delta\varepsilon_{\rm int,i}$ represents the interaction energy of H^+ on the electrode surface.

Here we assume that $\Delta\varepsilon_{\rm int,i}$ is negligibly small compared with $\Delta\varepsilon_{\rm int,f}$. Under this condition, we have

$$\Delta\varepsilon_{\rm fi} = \Delta\varepsilon_{\rm int,f} = \beta E_{\rm M-H} \tag{D8}$$

where $E_{\rm M-H}$ represents the adsorption energy of hydrogen on a metal surface in the vacuum. Parameter β represents the shielding factor by which the adsorption energy of hydrogen is shielded by a solvent layer near the electrode. This parameter was introduced here, because the adsorption energy of hydrogen in the vacuum $E_{\rm M-H}$ is thought to be weakened by a solvent layer near the electrode.

Here we define

$$I_0 = \frac{2\pi e}{\hbar} C_{\rm A} v^2 \rho(E_{\rm f}) \tag{D9}$$

$$\Delta E = \varepsilon_0 - \Delta\varepsilon_{\rm fi} + eV_{\rm eq} \tag{D10}$$

By using the relation of Eqs. D8, D9, and D10, the exchange current of hydrogen evolution $i_{0,\rm H}$ is expressed from Eq. 38 as,

$$i_{0,\rm H} = I_0 \exp - \frac{\Delta E}{kT} = I_0 \exp - \frac{(\varepsilon_0 - \Delta\varepsilon_{\rm fi} + eV_{\rm eq})}{kT} \tag{D11}$$

The exchange current of Eq. D11 is rewritten as,

$$\begin{aligned} i_{0,\rm H} &= I_0 \exp - \frac{(\varepsilon_0 + eV_{\rm eq})}{kT} \times \exp \frac{\Delta\varepsilon_{\rm fi}}{kT} \\ &= C \times \exp \frac{\Delta\varepsilon_{\rm fi}}{kT} = C \exp \frac{\beta E_{\rm M-H}}{kT} \end{aligned} \tag{D12}$$

$$\therefore \quad \log i_{0,\rm H} = C_1 + \frac{\beta E_{\rm M-H}}{2.303kT} \tag{D13}$$

where

$$C_1 = \log \left(I_0 \exp - \frac{(\varepsilon_0 + eV_{\rm eq})}{kT} \right) \tag{D14}$$

C_1 is a constant. Equation D13 indicates that $\log i_{0,\rm H}$ plotted against $E_{\rm M-H}$ should be on a straight line if the theory is correct.

Figure 6 shows the result of $\log i_{0,\rm H}$ plotted against $E_{\rm M-H}$ on various kind of metal electrodes.[12] It shows a volcano shaped dependence with its maximum of $\log i_{0,\rm H} = -3.0$ at $E_{\rm M-H} = 2.6$ eV for Pt. As is shown here, $\log i_{0,\rm H}$ values are on a straight line, as was already point out by Trasatti.[12]

This result supports Eq. D13. From the slope of the straight line at the left branch of Fig. 6, the value of β can be determined. The theoretical slope is $\frac{\beta}{2.3kT}$ from Eq. D13. The slope of the solid line in the left branch in Fig. 6 is 6.8 eV.

Consequently $\frac{\beta}{2.3kT} = 6.8$ eV.

From this equation

$$\beta = 0.40 \tag{D15}$$

is obtained. Next let's compare the magnitude of $i_{0,\rm H}$ at Pt electrode with that at Hg electrode. The adsorption energies of hydrogen on Pt and Hg are[13]

$$E_{\rm Hg-H} = 1.26\,\text{eV}, \qquad E_{\rm Pt-H} = 2.60\text{—}3.03\,\text{eV}$$

From Eq. D13 we get

$$\Delta \log i_{0,\rm H} \equiv \log i_{0,\rm H}(\text{Pt}) - \log i_{0,\rm H}(\text{Hg}) = \frac{\beta(E_{\rm Pt-H} - E_{\rm Hg-H})}{2.30kT} \tag{D16}$$

When we use $E_{\rm Pt-H} = 2.6$ eV, and $\beta = 0.40$, we get $\Delta\log i_{0,\rm H} = 9.1$ from Eq. D16. For $E_{\rm Pt-H} = 3.03$ eV and $\beta = 0.40$, we get $\Delta\log i_{0,\rm H} = 12.0$ from Eq. D16. Therefore,

$$\Delta \log i_{0,\rm H} = \log i_{0,\rm H}(\text{Pt}) - \log i_{0,\rm H}(\text{Hg}) = 12.0\text{—}9.1 \tag{D17}$$

is obtained.

On the other hand, the experimental value of $\Delta\log i_{0,\rm H}$ is about 9.3.[12] It agrees well with the calculated values of Eq. D17.

From the above discussion, it is concluded that the large $i_{0,\rm H}$ value at Pt electrode is caused by a large adsorption energy of hydrogen on Pt, i.e. $E_{\rm Pt-H}$. When $E_{\rm M-H}$ is large, $\Delta\varepsilon_{\rm fi}$ becomes large according to Eq. D8. For a large $\Delta\varepsilon_{\rm fi}$ the activation energy ΔE decreases (see Eq. D10). Then, $i_{0,\rm H}$ increases as seen from Eq. D11. On the other hand, $E_{\rm M-H}$ is small on Hg electrode. Therefore, ΔE becomes large, resulting in a small $i_{0,\rm H}$ on Hg electrode.

From the above discussion, it is concluded that the left branch ($E_{\rm M-H} \leq 2.6$ eV in Fig. 6) is the electorn transfer limited region. Equation 8 shows that $\Delta\varepsilon_{\rm fi}$ is cathodic "electron transfer adsorption". Consequently, in the left hand branch "electron transfer adsorption" plays very important role (see

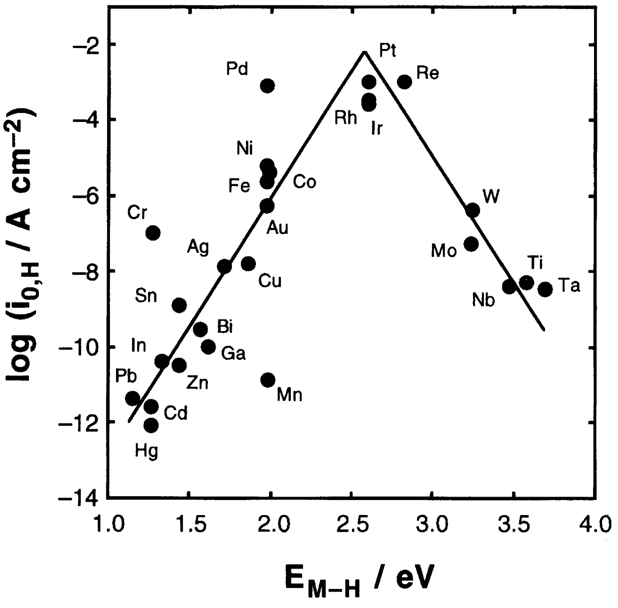

Fig. 6. Exchange currents for electrolytic hydrogen evolution vs. adsorption energy of hydrogen $E_{\rm M-H}$ on various metals. $E_{\rm M-H}$ from Krishtalik.[13]

Eqs. D8 and D13) in the left hand branch of Fig. 6. $\log i_{0,\mathrm{H}}$ in the right hand branch ($E_{\mathrm{M-H}} \geq 2.6$ eV in Fig. 6) is also on a straight line as shown in Fig. 6. How is this right region explained? This region is also related with the mechanism of hydrogen evolution, as follows. In the region of $E_{\mathrm{M-H}} \geq 2.6$ eV, desorption of ·H (hydrogen atom) from the electrode surface is considered to be the rate determining step, because of the large $E_{\mathrm{M-H}}$.

In this case, the reaction rate k would be expressed as,

$$k \propto \exp - \frac{\Delta G_{\mathrm{des}}}{kT} \tag{D18}$$

Here ΔG_{des} represents the free energy change of the desorption of hydrogen atom from the electorde surface which corresponds to the free energy change of the reaction (D6).

ΔG_{des} is expressed as,

$$\Delta G_{\mathrm{des}} = \Delta \varepsilon_{\mathrm{ad}} - \frac{1}{2} D(\mathrm{H\text{-}H}) \tag{D19}$$

Where D(H–H) is the bonding energy of H_2 and $\Delta \varepsilon_{\mathrm{ad}}$ is the adsorption energy of a hydrogen atom on the electrode. Since D(H–H)=4.48 eV, we obtain from Eq. D19

$$\Delta G_{\mathrm{des}} = \Delta \varepsilon_{\mathrm{ad}} - 2.24 \tag{D20}$$

By substituting Eq. D20 into Eq. D18, we obtain

$$k \propto \exp - \frac{\Delta \varepsilon_{\mathrm{ad}} - 2.24}{kT} \tag{D21}$$

Omitting the constant term, Eq. D21 yields

$$\log k \propto - \frac{\Delta \varepsilon_{\mathrm{ad}}}{2.3kT} \tag{D22}$$

Because $\log k$ is considered as $\log i_{0,\mathrm{H}}$, Eq. D22 is written as,

$$\log i_{0,\mathrm{H}} \propto - \frac{\Delta \varepsilon_{\mathrm{ad}}}{2.3kT} \tag{D23}$$

From Eq. D8,

$$\Delta \varepsilon_{\mathrm{ad}} = \Delta \varepsilon_{\mathrm{int}} = \beta E_{\mathrm{M-H}} \tag{D24}$$

Here β represents the shielding factor of the adsorption energy defined by Eq. D8. Substitution of Eq. D24 into Eq. D23 gives

$$\log i_{0,\mathrm{H}} \propto - \frac{\beta E_{\mathrm{M-H}}}{2.3kT} \tag{D25}$$

Equation D22 means that $\log i_{0,\mathrm{H}}$ is proportional to $E_{\mathrm{M-H}}$. The right branch of Fig. 6 is also on a straight line. The slope of the solid line in the right branch in Fig. 6 is −6.65 eV.

The slope of Eq. D25 is $-\frac{\beta}{2.3kT}$. The value of β determined from $\frac{\beta}{2.3kT}=6.65$ is $\beta=0.39$. Thus the right hand branch of Fig. 6 can be explained by the above theory. Moreover $\beta=0.39$ is very close to $\beta=0.40$ which was determined from the left branch of Fig. 6.

As shown in the above discussion, the volcano shaped dependence of $\log i_{0,\mathrm{H}}$ on $E_{\mathrm{M-H}}$ is related with a microscopic mechanism of hydrogen evolution and explained well by the present theory. The left hand side of Fig. 6, i.e. $E_{\mathrm{M-H}}<2.6$ eV, is the electron transfer limited region. Since hydrogen is adsorbed strongly on the metal surface with increasing $E_{\mathrm{M-H}}$, the desorption and recombination of hydrogen becomes the rate determining step in the right hand branch of Fig. 6, i.e. $E_{\mathrm{M-H}}>2.6$ eV. Thus, the above discussion leads us to the conclution that the rate determining step of the hydrogen evolution is the electron transfer step of Eq. D5 or the recombination step of Eq. D6 depending on the adsorption energy of hydrogen. The electrochemical mechanism of Eq. D7 can be ignored.

C) Theoretical Evaluation of the Exchange Current of the Hydrogen Evolution Reaction. In the present theory, the exchange current plays an important role. It is well known that the exchange current of hydrogen evolution change dramatically depending on the kind of metal electrode.[16,17] This problem was discussed by Trasatti et al.[12,15]

As was already discussed, the hydrogen evolution reaction is typical case of the weak coupling. Now we will discuss the exchange current of hydrogen evolution based on the present theory in the weak coupling case.

As seen from Eq. 38, for the theoretical evalution of the exchange current the value of the state density near the Fermi level, i.e. $\rho(E_{\mathrm{f}})$ is necessary.

In the electrode reaction Fermi level changes depending on the electrode potential.

From Eq. 18,

$$E_{\mathrm{f}} = -\mathrm{e}V \tag{18}$$

By dividing V into two components, Eq. 18 can be written as

$$E_{\mathrm{f}} = -\mathrm{e}(V_{\mathrm{f}} + V_{\mathrm{im}}) \tag{D26}$$

where V_{im} is the imposed potential (voltage) added on V_{f}. Here $-\mathrm{e}V_{\mathrm{f}}$ represents the Fermi energy in the absence of the imposed potential. In the free electron theory of metals, the Fermi energy is about several eV. For instance, 7.00 eV for Cu and 5.51 eV for Au[11] and 5.49 eV for Pt. From the free electron theory of metal, the state density is given by

$$\rho(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E} \tag{D27}$$

From Eqs. D26 and D27,

$$\rho(E_{\mathrm{f}}) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{-\mathrm{e}(V_{\mathrm{f}} + V_{\mathrm{im}})} \tag{D28}$$

The state density in the absence of imposed potential $\rho(E_{\mathrm{f}}^0)$ is from Eq. D28

$$\rho(E_{\mathrm{f}}^0) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{-\mathrm{e}V_{\mathrm{f}}} \tag{D29}$$

From Eqs. D28 and D29,

$$\frac{\rho(E_{\mathrm{f}})}{\rho(E_{\mathrm{f}}^0)} = \sqrt{\frac{V_{\mathrm{f}} + V_{\mathrm{im}}}{V_{\mathrm{f}}}} = \sqrt{1 + \frac{V_{\mathrm{im}}}{V_{\mathrm{f}}}} \tag{D30}$$

For $V_{\mathrm{im}}=1.0$ V,

$$\frac{\rho(E_{\mathrm{f}})}{\rho(E_{\mathrm{f}}^0)} = \sqrt{\frac{8.0}{7.0}} = 1.069 \tag{D31}$$

is calculated for Cu.

$\frac{\rho(E_f)}{\rho(E_f^0)}=1.087$ is calculated for Au and $\frac{\rho(E_f)}{\rho(E_f^0)}=1.081$ for Pt.

All the above calculations show that the effect of the imposed potential on the state density is small within the polarization less than 1.0 V. Therefore, $\rho(E_f^0)=\rho(E_f)$ assumed for the weak coupling case seems a good approximation. Therefore, hereafter we use the state density in the absence of imposed potential and write it $\rho(E_f)$. The state density $\rho(E_f)$ can be obtained from the electronic heat capacity of the metal as follows.

C-1). State Density and Electronic Heat Capacity. The heat capacity C_{el} of the electron gas in a metal is expressed as[11)]

$$C_{el} = \frac{1}{3}\pi^2\rho(E_f)k^2T \tag{D32}$$

$$\text{When } \gamma = \frac{1}{3}\pi^2\rho(E_f)k^2 \tag{D33}$$

is defined,

$$C_{el} = \gamma T \tag{D34}$$

Parameter γ is obtained experimentally from electronic heat capacity.[11)] From the relation of Eq. D32,

$$\rho(E_f) = \frac{3\gamma}{\pi^2k^2} \tag{D35}$$

is obtained. Therefore the state density at Fermi level $\rho(E_f)$ can be evaluated by using Eq. D35.

Table 1 shows the experimental value of γ^{11} and $\rho(E_f)$ in the absence of imposed potential for various metals calculation from Eq. D35.

C-2) Quantitative Caluculation of the Exchange Current for Hydrogen Evolution. $C_A=10^{20}$ molecules/cm^3 is assumed. This concentration corresponds to 1 M (1 M=1 mol dm^{-3}). The magnitude of electron exchange energy v is important for the calculation. However, its magnitude is unknown. Now, let's assume $v=10$ cm^{-1} tentatively.

We use $\rho(E_f)=1.82\times10^{12}$ erg^{-1}·molecule^{-1} for Pt from Table 1. Using these values, we obtain

$$I_0 = \frac{2\pi e}{\hbar}v^2\rho(E_f)C_A = 68.6\times10^{10}\text{A cm}^{-2} \tag{D36}$$

Next, let's assume $v=100$cm^{-1}.In this case, we obtain

$$I_0 = \frac{2\pi e}{\hbar}v^2\rho(E_f)C_A = 68.6\times10^{12}\text{A cm}^{-2} \tag{D37}$$

by a similar calculation. Next, left's evaluate ΔE and $\exp-\frac{\Delta E}{kT}$.

From Eqs. D8 and D15,

$$\Delta\varepsilon_{fi} = \Delta\varepsilon_{int,f} = \beta E_{M-H} = 0.40\,E_{M-H} \tag{D38}$$

When $E_{Pt-H}=2.60$ eV is used, $\Delta\varepsilon_{fi}=1.04$ eV is obtained.

Now let's evaluate the activation energy ΔE. For the evaluation the value of V_{eq} is necessary. V_{eq} contain a concentration term as seen in Eq. 27. Since this term is considered to be small, we might neglect it. Under this assumption,

$$V_{eq} = V_0 = V_{NHE} \tag{D39}$$

is obtained. Here eV_{NHE} represents the energy level of normal hydrogen electrode in the vaccum scale.

Table 1. Electronic Heat Capacity Constant γ (mJ mol^{-1} K^{-2}) and State Desity $\rho(E_f)$ of Various Metals.

Metal	γ	$\rho(E_f)$ (10^{11} molecule^{-1}K^{-2})
Ti	3.35	8.94
Cr	1.40	3.74
Mn	9.20	24.6
Fe	4.98	13.3
Co	4.73	12.7
Ni	7.02	18.7
Cu	0.695	1.86
Zn	0.64	1.71
Ga	0.596	1.59
Zr	2.80	7.48
Nb	7.79	20.8
Mo	2.0	5.34
Ru	3.3	8.81
Rh	4.9	13.1
Pd	9.42	25.2
Ag	0.646	1.72
Cd	0.688	1.84
In	1.69	4.51
Sn	1.78	4.75
Sb	0.11	0.3
Pt	6.8	18.2
Au	0.729	1.95
La	10.0	26.7
Hf	2.16	5.76
Ta	5.9	15.8
W	1.3	3.47
Re	2.3	6.14
Os	2.4	6.41
Ir	3.1	8.28
Hg	1.79	4.78
Tl	1.47	3.92
Pb	2.98	7.96
Bi	0.008	0.02

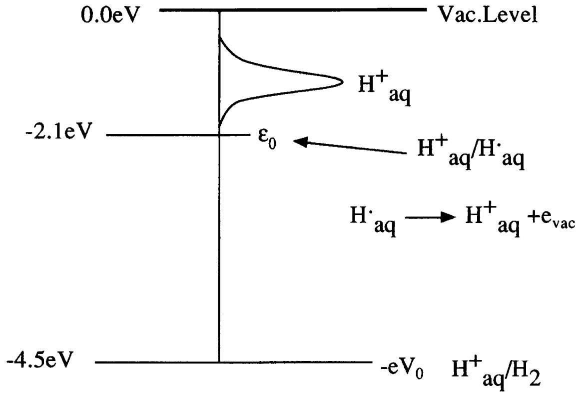

Fig. 7. A schematic illustration of ε_0 and eV_0 in the vacuum scale for hydrogen evolution reaction.

Now we use the following values ε_0[14)] and eV_{NHE},[16,18)] measuring energy level from the vacuum level, i.e. vacuum scale.

$$\varepsilon_0 = -2.1\text{ eV},\quad eV_{NHE} = 4.5\text{ eV} \tag{D40}$$

Figure 7 illustrates these energy levels in the vacuum scale. If we use these values,

$$\Delta E = 1.36\ \mathrm{eV} \qquad \text{(D41)}$$

is obtained from Eq. D10.

Using this value, we can calculate

$$\exp - \frac{\Delta E}{kT} = \exp - \frac{1.36}{0.0257} = 1.042 \times 10^{-23} \qquad \text{(D42)}$$

In the case of $v = 10\ \mathrm{cm}^{-1}$

$$i_{0,\mathrm{H}} = I_0 \exp - \frac{\Delta E}{kT} = 7.15 \times 10^{-12}\ \mathrm{A\,cm}^{-2} \qquad \text{(D43)}$$

is obtained from Eqs. D36 and D42. This value is too small compared with the experimental value.

In the case of $v = 100\ \mathrm{cm}^{-1}$,

$$i_{0,\mathrm{H}} = I_0 \exp - \frac{\Delta E}{kT} = 7.15 \times 10^{-10}\ \mathrm{A\,cm}^{-2} \qquad \text{(D44)}$$

is obtained from Eqs. D37 and D42. This value is still too small compared with the experimental value of mA at Pt.[12)]

In order to obtain the suitable value of mA, the electron exchange energy v should be increased much more than 100 cm^{-1}. However, this looks unrealistic. It seems reasonable to change the value of ΔE. Now let's assume $\varepsilon_0 = -2.4$ eV, $\Delta\varepsilon_{\mathrm{fi}} = 1.1$ eV and $eV_{\mathrm{NHE}} = 4.5$ eV.

Under this assumption, $\Delta E = \varepsilon_0 - \Delta\varepsilon_{\mathrm{fi}} + eV_{\mathrm{NHE}} = 1.0$ eV is obtained. When this value is used,

$$\exp - \frac{\Delta E}{kT} = 1.26 \times 10^{-17} \qquad \text{(D45)}$$

is obtained. In the case of $v = 100\ \mathrm{cm}^{-1}$,

$$i_{0,\mathrm{H}} = 0.86 \times 10^{-3}\ \mathrm{A\,cm}^{-2} \qquad \text{(D46)}$$

is obtained from Eqs. D37 and D45. This value is quite close to the experimental value 10^{-3} $\mathrm{A\,cm}^{-2}$.[12)]

As is seen in the above calculation, the exchange current can be calculated by the present theory, whereas in the classical theory it is impossible. The above calculation shows that accurate information about v and ΔE is important to obtain a reliable value of the exchange current. Especially information of ΔE is very important, because the exchange current depends very sensitively on the value of ΔE.

The value of $E_{\mathrm{Pt-H}}$ is in the range of 2.6—3.0 eV. If we use $E_{\mathrm{Pt-H}} = 3.0$ eV as the adsorption energy of hydrogen on Pt, $\Delta\varepsilon_{\mathrm{fi}} = 1.2$ eV is obtained. Therefore, $\Delta E = 1.0$ eV used in the calculation of Eq. D44 is possible. The activation energy ΔE is influenced sensitively by the evaluation of ε_0 and $\Delta\varepsilon_{\mathrm{fi}}$ as shown in the above calculation.

At present the literature data on the species involved are too fragmentary to solve the problem. If we can evaluate ΔE based on more reliable data, we could calculation the exchange current in a more accurate way.

The another important factor that affects the exchange current is the state density of the metal electrode $\rho(E_{\mathrm{f}})$. However, the change of the state density $\rho(E_{\mathrm{f}})$ is at most 1000 times, as seen in Table 1. This change is much smaller than the change of the hydrogen exchange current of 10^{10}. Moreover there is no clear correlation between the state density of Table 1 and the exchange cuurent.

Therefore the dependence of $\rho(E_{\mathrm{f}})$ on the kind of metal cannot explain the result of Fig. 6.

As is shown in the above discussion, the present theory can explain microscopically the mechanism of hydrogen evolution as well as the quantitative explanation of the exchange current, which can not be explained well by the classical theory.[1,17)]

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