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Author(s)	MATSUDA, Akiya; NOTOYA, Reiko
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EXCHANGE RATE OF ELECTRON TRANSFER STEP OF HYDROGEN ELECTRODE REACTION AT ISOELECTRIC CONDITIONS $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H}=1$ IN FRUMKIN'S ELECTRODE POTENTIAL THEORY

By

Akiya Matsuda[*] and Reiko Notoya[*]

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Abstract

The reversible hydrogen electrode potential on platinum was discussed on the basis of Frumkin's electrode potential theory. It was found that the electrode potential in acid solutions at the isoelectric conditions $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H}=1$ could be divided into two independent parts, *i.e.*, the potential due to free charges on the electrode surface and that due to adsorbed hydrogen atoms, and the former depended on μ_{H^+} and the latter on μ_H, where φ denoted the electrode potential, μ_{H^+} and μ_H the chemical potentials of proton in solution and adsorbed hydrogen atom H, and Γ_H the surface density of the adsorbed hydrogen atom in the sense of Gibbs thermodynamics.

Taking into consideration the functional relations of these two components of the hydrogen electrode potential, it was concluded that the exchange rate of the electron transfer step of the hydrogen evolution reaction was proportional to the square root of the activity of proton in solution.

Frumkin[1] has developed a theory on the setting up of the electrode potential on the basis of Gibbs thermodynamics in the reversible hydrogen electrode system in which the change of the charge density on the electrode surface ε occurs through the reaction:

$$H^+ + e \rightleftharpoons H, \tag{1}$$

where H is the adsorbed hydrogen atom. In this system the electrode potential is expressed thermodynamically by the equation:

$$d\varphi = d\mu_{H^+} - d\mu_H, \tag{2}$$

and

$$d\varphi_r = -d\mu_H, \tag{3}$$

where φ and φ_r denote the electrode potentials referred respectively to the

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*) Research Institute for Catalysis, Hokkaido Univ., Sapporo, Japan.

normal hydrogen electrode and the reversible hydrogen electrode in the same solution under the atmospheric pressure of hydrogen, and μ_{H^+} and μ_H the chemical potentials of H^+ and H expressed in terms of the electric unit.

FRUMKIN's theory will first be introduced in what follows.

The quantity of adsorbed hydrogen atoms in the sense of Gibbs thermodynamics Γ_H is expressed by the equation:

$$\Gamma_H = A_H - \varepsilon , \tag{4}$$

where A_H is the quantity of adsorbed hydrogen atoms on the electrode surface per unit area expressed in terms of the electric unit. Γ_H shows the total charge stored on the electrode surface, inasmuch as the ionization of H results in the appearance of the negative charge on the electrode surface. The conditions in which Γ_H is kept constant are called the isoelectric conditions in FRUMKIN's theory.

In acidified neutral salt solutions in which the concentration of salt is much higher than that of acid and remains constant, the states of the system can be determined by the independent variables μ_{H^+} and μ_H. In such a system the adsorbed quantity of H^+ in the sense of Gibbs thermodynamics Γ_{H^+} is shown to be equal to ε:

$$\Gamma_{H^+} = \varepsilon , \tag{5}$$

and a fundamental relation between Γ_H and Γ_{H^+} can be deduced from Gibbs adsorption equation[1]:

$$(\delta\Gamma_H/\delta\mu_{H^+})_{\mu_H} = (\delta\Gamma_{H^+}/\delta\mu_H)_{\mu_{H^+}} . \tag{6}$$

The pH-dependence of the hydrogen electrode potential at the isoelectric conditions is obtained, taking into consideration Eqs. (2), (3) and (6):

$$(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H} = (\delta\varphi_r/\delta\mu_{H^+})_{\Gamma_H} + 1 ,$$
$$= (\delta\Gamma_{H^+}/\delta\varphi_r)_{\mu_{H^+}} / (\delta\Gamma_H/\delta\varphi_r)_{\mu_{H^+}} + 1 , \tag{7}$$

since Γ_H is a function of μ_{H^+} and μ_H.

A number of experimental results on $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H}$ on metals of platinum group obtained by FRUMKIN and his school[2-7] show a good coincidence with those calculated by Eq. (7) from the charging curves (Γ_H, φ_r-curves)[8] and the adsorption curves (Γ_{H^+}, φ-curves).[9,10] Thus it has been established by FRUMKIN and his school that the mechanism of the setting up of the hydrogen electrode potential in the reversible systems can be clarified on the basis of Gibbs thermodynamics. Furthermore they have shown that it is possible to divide the electrode potential into two parts, i.e., the one due to A_H and the other due to ε,[12,13]

$$d\varphi = (\delta\varphi/\delta A_H)_\varepsilon dA_H + (\delta\varphi/\delta\varepsilon)_{A_H} d\varepsilon = X dA_H + Y d\varepsilon ,\qquad(8)$$

where

$$X \equiv (\delta\varphi/\delta A_H)_\varepsilon , \qquad Y \equiv (\delta\varphi/\delta\varepsilon)_{A_H} ,\qquad(9\,a),\ (9\,b)$$

The reciprocals of X and Y mean the differential capacities respectively due to A_H and ε, which can be determined experimentally from the charging and adsorption curves.[14,15]

According to the experimental results of FRUMKIN school, $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H}$ practically equals unity at potentials close to the reversible hydrogen electrode potential under the atmospheric pressure in every case of platinum group metals independent of the composition of solution. The setting up of the electrode potential at the conditions $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H}=1$ is of special interest, since in this case $X dA_H$ and $Y d\varepsilon$ are shown to be mutually independent when $|Y| \gg |X|$, as will be shown later, so that it may be possible in this case to find which part of potential of these two is responsible for the rate of the electron transfer step (1). The present paper is concerned with a trial to find the pH-dependence of the exchange rate of the electron transfer reaction (1) at the isoelectric conditions $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H}=1$ on the basis of the electrode potential theory of FRUMKIN, assuming that the rate of the electron transfer step depends only on the potential set up by free charges on the electrode surface.

It can be seen from Eq. (7) that the condition $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H}=1$ means the constancy of ε independent of φ_r or $(\delta\Gamma_{H^+}/\delta\varphi_r)_{\mu_{H^+}}=0$, as pointed out by FRUMKIN. It follows from Eq. (6) that:

$$(\delta\Gamma_H/\delta\mu_{H^+})_{\mu_H} = (\delta\Gamma_{H^+}/\delta\mu_H)_{\mu_{H^+}} = 0 ,\qquad(10)$$

On the other hand, A_H and ε are functions of μ_H and μ_{H^+}. It follows that:

$$X dA_H = X(\delta A_H/\delta\mu_H)_{\mu_{H^+}} d\mu_H + X(\delta A_H/\delta\mu_{H^+})_{\mu_H} d\mu_{H^+} ,\qquad(11)$$

$$Y d\varepsilon = Y(\delta\varepsilon/\delta\mu_H)_{\mu_{H^+}} d\mu_H + Y(\delta\varepsilon/\delta\mu_{H^+})_{\mu_H} d\mu_{H^+} ,\qquad(12)$$

From Eqs. (2) and (8), we obtain:

$$X(\delta A_H/\delta\mu_H)_{\mu_{H^+}} + Y(\delta\varepsilon/\delta\mu_H)_{\mu_{H^+}} = -1 ,\qquad(13)$$

$$X(\delta A_H/\delta\mu_{H^+})_{\mu_H} + Y(\delta\varepsilon/\delta\mu_{H^+})_{\mu_H} = 1 ,\qquad(14)$$

Putting Eq. (10) into Eqs. (13) and (14), and taking into consideration Eq. (4), we obtain:

$$X(\delta A_H/\delta\mu_H)_{\mu_{H^+}} = -1 ,\qquad(15)$$

$$(X + Y)\,(\delta\varepsilon/\delta\mu_{H^+})_{\mu_H} = 1 ,\qquad(16)$$

Putting Eqs. (15) and (16) into Eqs. (11) and (12), and taking into consideration Eqs. (10) and (4), we obtain:

$$X dA_H = -d\mu_H + \frac{X}{X+Y} d\mu_{H^+} , \qquad (17)$$

$$Y d\varepsilon = \frac{Y}{X+Y} d\mu_{H^+} , \qquad (18)$$

If we assume here that $|Y| \gg |X|$, as realized in the case of platinum group metals,[13,15] then we have from Eqs. (17) and (18):

$$X dA_H = -d\mu_H , \qquad (19)$$

$$Y d\varepsilon = d\mu_{H^+} , \qquad (20)$$

It can readily be seen that the summation of Eqs. (17) and (18) or (19) and (20) satisfies the thermodynamic relation (2). Eqs. (19) and (20) show that the change of the electrode potential due to A_H depends only on μ_H and that due to ε only on μ_{H^+}, i.e., the electrode potential can be divided into two independent parts in the case $|Y| \gg |X|$ at the isoelectric conditions $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H} = 1$. Let us denote in this case $Y d\varepsilon \equiv d\varphi_1$ and $X dA_H \equiv d\varphi_2$, then we have from Eqs. (19) and (20):

$$\varphi_1 = (RT/F) \ln a_{H^+} + \text{const.} \qquad (21)$$

$$\varphi_2 = -(RT/F) \ln a_H + \text{const.} \qquad (22)$$

and

$$\varphi = \varphi_1 + \varphi_2 , \qquad (23)$$

where a_{H^+} and a_H are the activities of H^+ and H.

If we assume here that the rate of the electron transfer reaction i_1 depends only on φ_1 independent of φ_2 and can be expressed by simplified FRUMKIN equation omitted Ψ_1-potential term, then the exchange rate of the reaction i_{10} can be written as:

$$i_{10} = k(a_{H^+}) \exp(-\alpha F\varphi_1/RT) , \qquad (24)$$

where k and α are constants. Putting Eq. (21) into (24), we obtain:

$$i_{10} = \text{const} \cdot (a_{H^+})^{1-\alpha} . \qquad (25)$$

It can be seen from Eq. (25) that the exchange rate of the electron transfer step is proportional to the square root of a_{H^+} when α equals 1/2.

If we assume that even in the irreversible states of the hydrogen electrode reaction the electrode potential consists of two independent parts φ_1 and φ_2

and the latter is expressed by Eq. (22), then i_1 is expressed by FRUMKIN equation on the assumption that the rate of the electron transfer step depends only on φ_1 independent of φ_2:

$$i_1 = k_1'(a_{H^+}) \exp(-\alpha F\varphi_1/RT) - k_2' \exp(\beta F\varphi_1/RT), \qquad (26)$$

where k_1' and k_2' are constants and $\alpha + \beta = 1$. Putting $\varphi_1 = \varphi - \varphi_2$ into Eq. (26), we have:

$$i_1 = k_1'(a_{H^+}) \exp\left\{-\alpha F(\varphi - \varphi_2)/RT\right\} - k_2' \exp\left\{\beta F(\varphi - \varphi_2)/RT\right\}, \quad (27)$$

Putting Eq. (22) into (27), we obtain:

$$i_1 = k_1''(a_{H^+})(a_H)^{-\alpha} \exp(-\alpha F\varphi/RT) - k_2''(a_H)^\beta \exp(\beta F\varphi/RT), \qquad (28)$$

where k_1'' and k_2'' are constants. If we assume a_H to be proportional to $\exp(f\theta)$ in accordance with FRUMKIN and ALADJALOVA[17], we obtain from Eq. (28):

$$i_1 = k_1(a_{H^+}) \exp(-\alpha f\theta) \exp(-\alpha F\varphi/RT) - k_2 \exp(\beta f\theta) \exp(\beta F\varphi/RT), \tag{29}$$

where k_1, k_2 and f are constants and θ the surface coverage of adsorbed hydrogen atoms. Comparing Eq. (29) and the rate equation obtained by FRUMKIN and ALADJALOVA,[17] it can be seen that both equations are idenitcal. This fact suggests that in the case of palladium hydrogen electrode worked out by FRUMKIN and ALADJALOVA, the isoelectric condition $(\delta\varphi/\delta\mu_{H^+})_{\Gamma_H}$ may be equal to unity and $|Y| \gg |X|$, and the hydrogen overvoltage may consist of two independent parts φ_1 and φ_2.

FRUMKIN's electrode potential theory in the reversible systems applies extensively to the setting up of the hydrogen overvoltage in the irreversible systems, which will be discussed later with reference to the platinum hydrogen electrode in alkaline solutions.

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