ON THE RELATION BETWEEN FORWARD
AND REVERSE UNI-DIRECTIONAL RATES OF
THE HYDROGEN ELECTRODE REACTION
IN ISOTOPICALLY MIXED SYSTEM

By

Michio ENYO*

(Received May 28, 1974)

Abstract

A relationship between the ratio of the forward uni-directional rate to the reverse one and overpotential of the hydrogen electrode reaction in isotopically mixed system was analyzed for the discharge-combination reaction route devoid of single rate-determining step. An exponential relation involving a mean stoichiometric number approximately holds near the isotopic mixed potential. An expression for the isotopic mixed potential in terms of isotope effects was also discussed.

Introduction

The overall forward and reverse uni-directional rates in c.d. unit, i_+, and i_-, of the hydrogen electrode reaction (HER),

$$H_2 + 2B = 2H^+B + 2e \qquad (1)$$

where $B = H_2O$ or OH^-, are related to its overpotential η, provided that a single rate-determining step (rds) exists,

$$i_+/i_- = \exp\{2f\eta/\nu_r\} \qquad (2)$$

where $f \equiv F/RT$ and ν_r is the stoichiometric number of the rds. This relation is utilized frequently in the studies of the HER mechanism through determination of ν_r from experimental observation of i_+ (or i_-) by means of an isotope tracer.

In order to proceed along this line, it is essential that a relation of the type of Eq. (2) is confirmed in the isotopically mixed system, even in case the isotope effect is significant. It has been shown previously[1] that such a relation holds with a sufficient accuracy if one defines η in Eq. (2) as the potential of the test electrode referred to the *rest* potential (the

---

* The Research Institute for Catalysis, Hokkaido University, Sapporo, Japan.

isotopic mixed potential, see below) of the same electrode in that system, rather than its original definition (in isotopically pure light hydrogen system) *i.e.* the potential referred to the *reversible* hydrogen electrode potential. A basic assumption was that a single rds exists in the reaction mechanism.

According to recent investigations, however, the HER on various metals takes place through the discharge-combination route but no single rds generally exists[2]. The relation analogous to Eq. (2) in such "coupled-controlled" cases will be discussed below.

Basic Relations

For a single-route reaction consisting of $1 \cdots s \cdots S$ consecutive steps, the free energy decrease (the reaction affinity) $-\Delta G$ is given by

$$-\Delta G = -\sum_s \nu_s \Delta g_s \qquad (3)$$

where $-\Delta g_s$ is the free energy decrease of step s. The forward uni-directional rate V_+ and the reverse one V_- of the overall reaction are related to those of the constituent steps, v_{+s} and v_{-s}, by[3,4]

$$\frac{V_+}{V_-} = \prod_s \frac{v_{+s}}{v_{-s}} \qquad (4)$$

and the latter rates are related to $-\Delta g_s$ by

$$v_{+s}/v_{-s} = \exp\{-\Delta g_s/RT\} \qquad (5)$$

In the case that an overwhelming rds, r, exists, *i.e.* all the other steps are in partial equilibrium, Eqs. (3) and (4) are reduced, respectively, to well-known relations,

$$-\Delta G = -\nu_r \Delta g_r \qquad (6)$$

and $\qquad V_+/V_- = v_{+r}/v_{-r} \qquad (7)$

or, according to Eq. (5),

$$V_+/V_- = \exp\{-\Delta G/\nu_r RT\} \qquad (8)$$

Analogously, in case no overwhelming rds exists, Eqs. (3)–(5) readily yield,

$$V_+/V_- = \exp\{-\Delta G/\bar{\nu} RT\} \qquad (9)$$

where $\bar{\nu}$ is defined by[4]

$$\bar{\nu} \equiv \sum_s \nu_s \Delta g_s / \sum_s \Delta g_s \qquad (10)$$

which may be called the "mean" stoichiometric number. These relations

are used to evaluate $\bar{\nu}$ from V_+ which is observed experimentally, usually employing an isotope tracer. However, the isotope effect then interferes with analysis of the experimental data, especially when such a light-mass elememt as hydrogen is involved.

Uni-directional Rates

We consider below the system consisting of a solution prepared from light water, gaseous hydrogen of an arbitrary deuterium concentration, and a test electrode. It will be assumed throughout the following analysis that the HER takes place through the discharge-combination route[2],

$$\text{step 1} \qquad\qquad \text{step 2}$$
$$H_2 \;\rightleftharpoons\; 2H(a), \; H(a)+B \;\rightleftharpoons\; H^+B+e \qquad\qquad (11)$$

The forward partial rate U_+^H of the overall HER for light hydrogen (H) under steady-state condition is given by[3,4]

$$U_+^H = u_{+1}^H u_{+2}^H / (u_{-1}^H + u_{+2}^H) \qquad\qquad (12)$$

and similarly the reverse one, U_-^H

$$U_-^H = u_{-1}^H u_{-2}^H / (u_{-1}^H + u_{+2}^H) \qquad\qquad (13)$$

where U_+^H, u_{+1}^H etc. are defined in terms of number of H atoms transferred per unit time. From Eqs. (12) and (13),

$$U_+^H / U_-^H = u_{+1}^H u_{+2}^H / u_{-1}^H u_{-2}^H \qquad\qquad (14)$$

Analogous expressions may be written for various partial rates for deuterium (D). The net rate U is given by

$$U = U_+ - U_- = U_+^H + U_+^D - (U_-^H + U_-^D) \qquad\qquad (15)$$

We define the deuterium separation factors as below.

$$S_+ = \frac{U_+^H}{1-X} \bigg/ \frac{U_+^D}{X} \quad \text{and} \quad S_- = \frac{U_-^H}{1-Z} \bigg/ \frac{U_-^D}{Z} \qquad\qquad (16, 17)$$

where X and Z are, respectively, the deuterium atomic fraction in the gaseous hydrogen and in the solution: In our system, $Z \simeq 0$. Accordingly, Eq. (15) is rewritten, using Eqs. (14), (16), and (17),

$$\frac{U}{U_-^H} = \frac{U_+^H}{U_-^H}\left(1 + \frac{1}{S_+'}\right) - \left(1 + \frac{1}{S_-'}\right) \qquad\qquad (18)$$

where

$$S_+' = (1-X)S_+/X \quad \text{and} \quad S_-' = (1-Z)S_-/Z \qquad\qquad (19, 20)$$

Rate ratio u_{+1}^H/u_{-1}^H in Eq. (14) is expressed as

$$\frac{u_{+1}^H}{u_{-1}^H} = \frac{2v_{+1}^{H_2} + v_{+1}^{HD}}{2v_{-1}^{H_2} + v_{-1}^{HD}} = \frac{v_{+1}^{H_2}}{v_{-1}^{H_2}} A \tag{21}$$

where $v_{+1}^{H_2}$ *etc.* are forward uni-directional rate of step 1 for the reaction of light hydrogen molecule, H_2, *etc.* given in number of times of occurrence of the step per unit time and,

$$A \equiv \frac{1 + v_{+1}^{HD}/2v_{+1}^{H_2}}{1 + v_{-1}^{HD}/2v_{-1}^{H_2}} = \frac{1 + X^{HD}/2\sigma_{+23}X^{H_2}}{1 + Y/\sigma_{-23}(1-Y)} \tag{22}$$

Here, X^{H_2} *etc.* are mole fractions of H_2 *etc.* in the gaseous hydrogen, Y is deuterium atomic fraction in hydrogen adatoms and σ_{+23} and σ_{-23} are the separation factors defined for HD molecule as

$$\sigma_{+23} = \frac{v_{+1}^{H_2}}{X^{H_2}} \Big/ \frac{v_{+1}^{HD}}{X^{HD}} \tag{23}$$

and

$$\sigma_{-23} = \frac{v_{-1}^{H_2}}{(1-Y)^2} \Big/ \frac{v_{-1}^{HD}}{2Y(1-Y)} \tag{24}$$

Similar to Eq. (21), we have

$$u_{+2}^H/u_{-2}^H = v_{+2}^H/v_{-2}^H \tag{25}$$

Substitution of Eqs. (14), (21) and (25) into Eq. (18) yields,

$$\frac{U}{U_-^H} = \frac{v_{+1}^{H_2}v_{+2}^H}{v_{-1}^{H_2}v_{-2}^H} A\left(1 + \frac{1}{S_+'}\right) - \left(1 - \frac{1}{S_-'}\right)$$

or using Eq. (5) and expressing in terms of chemical potentials,

$$\frac{U}{U_-^H} = A\left(1 + \frac{1}{S_+'}\right)\exp\left\{\frac{\mu^{H_2} - \mu^H - \mu^{H^+} - \mu^e}{RT}\right\} - \left(1 + \frac{1}{S_-'}\right) \tag{26}$$

At the rest potential (subscript R) at which $U=0$,

$$A_R(1 + 1/S_{+,R}')\exp\left\{(\mu^{H_2} - \mu_R^H - \mu^{H^+} - \mu_R^e)/RT\right\} = 1 + 1/S_{-,R}' \tag{27}$$

where μ^{H_2} and μ^{H^+} are taken to be constant independent of electrode potential and,

$$A_R = \frac{1 + X^{HD}/2\sigma_{+23}X^{H_2}}{1 + Y_R/\sigma_{-23}(1-Y_R)} \tag{28}$$

Eliminating μ^{H_2} and μ^{H^+} from Eqs. (26) and (27),

$$\frac{U}{U_-^{\mathrm{H}}} = \frac{A}{A_R} \frac{1+1/S'_{-,R}}{1+1/S'_{+,R}} \left(1+\frac{1}{S'_+}\right) \exp\left\{-\frac{\mu^{\mathrm{H}}-\mu_R^{\mathrm{H}}}{RT}\right\} \exp\left\{-\frac{\mu^{\mathrm{e}}-\mu_R^{\mathrm{e}}}{RT}\right\}$$
$$- \left(1+\frac{1}{S'_-}\right)$$

or, equating this with Eq. (18),

$$\frac{U_+^{\mathrm{H}}}{U_-^{\mathrm{H}}} \frac{1+1/S'_{+,R}}{1+1/S'_{-,R}} = \frac{U_+}{U_-} = \frac{A}{A_R} \frac{a_R^{\mathrm{H}}}{a^{\mathrm{H}}} \exp\{f\eta\} \tag{29}$$

where a^{H} denotes activity of H(a) and overpotental η is defined by

$$\eta = -(\mu^{\mathrm{e}}-\mu_R^{\mathrm{e}})/F \tag{30}$$

The first equality of Eq. (29) holds if S_+ and S_- are potential inpendent, which may approximately be valid in relatively a narrow potential region.

The right-hand side of Eq. (29) can be developed as follows. By the definition of A and of Y in terms of surface coverage θ,

$$\frac{A}{A_R} = \frac{1+Y_R/\sigma_{-23}(1-Y_R)}{1+Y/\sigma_{-23}(1-Y)} = \frac{1+\theta_R^{\mathrm{D}}/\sigma_{-23}\theta_R^{\mathrm{H}}}{1+\theta^{\mathrm{D}}/\sigma_{-23}\theta^{\mathrm{H}}} \tag{31}$$

Approximating the activity coefficient of H(a) in the mixture H(a)+D(a) to be equal to that of D(a) and further the coefficients to be composition-independent, we obtain from Eq. (31),

$$\frac{A}{A_R} \frac{a_R^{\mathrm{H}}}{a^{\mathrm{H}}} = \frac{B_R}{B} \frac{\theta_R^{(\mathrm{H+D})}}{\theta^{(\mathrm{H+D})}} \tag{32}$$

where $\theta^{(\mathrm{H+D})} \equiv \theta^{\mathrm{H}}+\theta^{\mathrm{D}}$ and

$$\frac{B_R}{B} \equiv \frac{1-(1-1/\sigma_{-23})Y_R}{1-(1-1/\sigma_{-23})Y} \tag{33}$$

The free energy decrease $-\varDelta g_1$, of step 1 may be given approximately as

$$-\varDelta g_1 = \mu^{(\mathrm{H+D})_2} - 2\mu^{(\mathrm{H+D})}$$

where $\mu^{(\mathrm{H+D})_2}$ denotes chemical potential of molecular hydrogen comprizing all the isotope components, H_2, HD, and D_2, and $\mu^{(\mathrm{H+D})}$ that of H(a)+D(a). At the rest potential, $\varDelta g_1=0$, or $\mu^{(\mathrm{H+D})_2}-2\mu_R^{(\mathrm{H+D})}=0$. Hence,

$$-\varDelta g_1 = -2\{\mu^{(\mathrm{H+D})}-\mu_R^{(\mathrm{H+D})}\} = -2RT\ln\theta^{(\mathrm{H+D})}/\theta_R^{(\mathrm{H+D})} \tag{34}$$

From Eq. (3) and

$$-\varDelta G = 2F\eta \tag{35}$$

we have,

$$-\Delta g_1 = 2mF\eta/(m+2) \tag{36}$$

where

$$m \equiv \Delta g_1/\Delta g_2 \tag{37}$$

Hence, Eq. (34) yields

$$-mF\eta/(m+2) = RT \ln \theta^{(\mathrm{H+D})}/\theta_R^{(\mathrm{H+D})} \tag{38}$$

Equation (29) is thus rewritten, using Eqs. (32) and (38),

$$U_+/U_- = (B_R/B) \exp \{2f\eta/\bar{\nu}\} \tag{39}$$

where, referring to Eq. (10), $\bar{\nu}$ is given as a function of m,

$$\bar{\nu} = (m+2)/(m+1) \tag{40}$$

Coefficient (B_R/B), Eq. (33), equals unity at the isotopic mixed potential. Also, it equals unity if $\sigma_{-23}=1$ which is found to be indeed approximately the case[5,6,*]. Thus, we may conclude that Eq. (9) derived for isotopically pure system holds also in the isotopically mixed hydrogen electrode system even in the absence of a single rds. Evaluation of $\bar{\nu}$ on the basis of Eq. (9) is thus justified. However, as stated above in connection with Eq. (29), the relation is not assured in the potential region far apart from the mixed potential. Another factor which may also invalidates Eq. (9) under highly irreversible condition is the change of the mechanism (hence variation of $\bar{\nu}$) with η in case devoid of an overwhelming rds, but this can be shown to be rather insignificant since m exhibits only slight variation with η in case m around the reversible potential is of the order of magnitude of unity[7].

Isotopic Mixed Potential

Potential of the hydrogen electrode placed in the system composed of deuterium and electrolytic solution prepared from light water is generally different from the reversible hydrogen electrode potential owing to the isotope effect[8]. This may be termed as the isotopic mixed potential as it is established on the compromise between ionization rate of deuterium and evolution rate of light hydrogen.

For the reversible hydrogen electrode in pure light hydrogen system (subscript o)

$$\mu_o^{\mathrm{H_2}} = 2\mu^{\mathrm{H^+}} + 2\mu_o^{\mathrm{e}} = \mu_o^{\mathrm{H}} + \mu^{\mathrm{H^+}} + \mu_o^{\mathrm{e}}$$

*) $B_R/B=1$ in case $Y, Y_R \simeq 1$ or $Y, Y_R \ll 1$. These conditions correspond, respectively, to the case that step 2 or 1 is singly rate-determining.

Substituting this into Eq. (27), we obtain

$$A_R(1+1/S'_{+,R}) \exp\left\{(\mu^{H_2}-\mu_o^{H_2}-\mu_R^H+\mu_o^H-\mu_R^e+\mu_o^e)/RT\right\} = 1+1/S'_{-,R} \tag{41}$$

Since $X_o^{H_2}=1$, $\exp\left\{(\mu^{H_2}-\mu_o^{H_2})/RT\right\}=X^{H_2}$. Denoting the activity of H(a) in the isotopically mixed system but at potential of the reversible hydrogen electrode in pure light hydrogen system (subscript $E=0$) as $a_{E=0}^H$, we have

$$\exp\left\{-\frac{\mu_R^H-\mu_o^H}{RT}\right\} = \frac{a_{E=0}^H}{a_R^H}\frac{a_o^H}{a_{E=0}^H}$$

in which the second factor in the right-hand side is $a_o^H/a_{E=0}^H = 1/(1-Y_{E=0})$. Employing these relations, Eq. (41) is rewritten as,

$$A_R\frac{1+1/S'_{+,R}}{1+1/S'_{-,R}}\frac{X^{H_2}}{1-Y_{E=0}}\frac{a_{E=0}^H}{a_R^H} = \exp\left\{-fE_R\right\} \tag{42}$$

where E_R is the isotopic mixed potential defined by,

$$E_R = -(\mu_R^e-\mu_o^e)/F \tag{43}$$

From Eq. (32) at $E=0$,

$$A_R\frac{a_{E=0}^H}{a_R^H} = A_{E=0}\frac{B_{E=0}}{B_R}\frac{\theta_{E=0}^{(H+D)}}{\theta_R^{(H+D)}}$$

or, using Eqs. (22), (33), and (38) and identifying $\eta_{E=0}=-E_R$,

$$A_R\frac{a_{E=0}^H}{a_R^H} = \frac{1+X^{HD}/2\sigma_{+23}X^{H_2}}{1+Y_{E=0}/\sigma_{-23}(1-Y_{E=0})}\frac{1-(1-1/\sigma_{-23})Y_{E=0}}{1-(1-1/\sigma_{-23})Y_R}\exp\left\{\frac{mfE_R}{m+2}\right\} \tag{44}$$

Equations (40) and (42) thus yield,

$$\exp\left\{-\frac{2fE_R}{\bar{\nu}}\right\} = \frac{1+1/S'_{+,R}}{1+1/S'_{-,R}}X^{H_2}\frac{1+X^{HD}/2\sigma_{+23}X^{H_2}}{1-(1-1/\sigma_{-23})Y_R} \tag{45}$$

The mole fractions can conveniently be expressed in terms of X as[8]

$$\left.\begin{array}{l} X^{H_2} = (1-X)(1-\rho X) \\ X^{HD} = 2\rho X(1-X) \\ X^{D_2} = X(1-\rho+\rho X) \end{array}\right\} \tag{46}$$

where

$$\rho \equiv X^{HD}/X_{K=4}^{HD} \tag{47}$$

and $X_{K=4}^{HD}$ signifies X^{HD} under random distribution of hydrogen isotopes in

the gas phase with respect to the isotopic equilibration reaction,

$$H_2 + D_2 = 2\,HD \tag{48}$$

Equation (45) now yields, using Eqs. (19) and (20) with $Z=0$,

$$\exp\left\{-\frac{2fE_R}{\bar{\nu}}\right\} = \left(1 - X + \frac{X}{S_{+,R}}\right)\frac{1 - (1 - 1/\sigma_{+23})\rho X}{1 - (1 - 1/\sigma_{-23})Y_R}$$

or,

$$\exp\left\{-fE_R\right\} = (1 - X + X/S_{+,R})C \tag{49}$$

where

$$C \equiv \left[\frac{1 - (1 - 1/\sigma_{+23})\rho X}{1 - (1 - 1/\sigma_{-23})Y_R}\right]^{\frac{\bar{\nu}}{2}}\left(1 - X + \frac{X}{S_{+,R}}\right)^{\left(\frac{\bar{\nu}}{2} - 1\right)} \tag{50}$$

It can be shown that Y_R is approximately given by[2]

$$Y_R = X/(m_R + 1)$$

or, according to Eq. (40)

$$Y_R = (\bar{\nu}_R - 1)X \tag{51}$$

Hence, Eq. (50) becomes

$$C = \left[\frac{1 - (1 - 1/\sigma_{+23})\rho X}{1 - (1 - 1/\sigma_{-23})(\bar{\nu}_R - 1)X}\right]^{\frac{\bar{\nu}_R}{2}}\left[1 - X + \frac{X}{S_{+,R}}\right]^{\left(\frac{\bar{\nu}_R}{2} - 1\right)} \tag{52}$$

At limiting cases of $\bar{\nu}_R = 1$ or 2, exact calculations lead to[8]

$$C_2 = \left[\frac{1 - \rho X}{1 - X}\right]^{1/2} \tag{53}$$

for $\bar{\nu}_R = 2$ and

$$C_1 = \left[\frac{1 - (1 - 1/S_{+,R})\rho X}{1 - (1 - 1/S_{+,R})X}\right]^{1/2} \tag{54}$$

for $\bar{\nu}_R = 1$. Equation (52) does not exactly yield these limiting values as it is of an approximate form, but nevertheless it shows the behaviour of C at intermediate values of $\bar{\nu}_R$. It can be shown that C is a monotonous function of $\bar{\nu}_R$, *i.e.*, it must take values between C_1 and C_2 at intermediate values of $\bar{\nu}_R$. Accordingly, within the error limit of $(C_2 - C_1)/C_1$ which is approximately 10% at $X=1$ (or less at $X<1$)[8], we may equate C to unity in Eq. (49), and thus directly evaluate $S_{+,R}$ from E_R. In case $\bar{\nu}_R$ is known beforehand and one has some information on σ_{+23} and σ_{-23}, one can improve the accuracy by taking contributions of C into account.

M. ENYO

References

1) M. ENYO and T. YOKOYAMA, Electrochim. Acta, **12,** 1631 (1967).
2) T. MATSUSHIMA, Dissertation, Hokkaido Univ., 1971.
   T. MATSUSHIMA and M. ENYO, Electrochim. Acta, **19,** 117, 125, 131 (1974).
3) A. MATSUDA and J. HORIUTI, This Journal, **10,** 14 (1962).
4) M. I. TEMKIN, Doklady Akad. Nauk, SSSR, **152,** 156 (1963).
5) T. YOKOYAMA and M. ENYO, This Journal, **15,** 207 (1967).
6) M. ENYO, to be published.
7) M. ENYO, Electrochim. Acta, **18,** 155 (1973).
8) M . ENYO and T. YOKOYAMA, Electrochim. Acta, **12,** 1641 (1967).