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A GENERAL RELATION BETWEEN FORWARD AND BACKWARD ISOTOPE SEPARATION FACTORS IN THE HYDROGEN ELECTRODE REACTION

By

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Abstract

A general relation is derived between two electrolytic hydrogen-deuterium separation factors, S_f and S_b, respectively in the hydrogen evolution and ionization reactions on one and the same electrode in the system composed of "light" water (containing deuterium of the natural abundance) and hydrogen gas at any deuterium atomic fraction X^G.

The relation was found to depend on the value of ν, the stoichiometric number of the rate-determining step of the hydrogen electrode reaction. In the case of $\nu=1$, S_f is given as $S_f=Q_{L-G,o}\cdot\sigma_{23}$ at any X^G-value, where $Q_{L-G,o}$ is the partition coefficient of deuterium between aqueous solution and hydrogen gas at $X^G\simeq 0$ and σ_{23} is the ratio of specific rate of ionization of H_2 to that of HD; the latter is determined from S_b. In the case of $\nu=2$, the relation is $S_f=Q_{L-G,o}\cdot S_b(m^{HD}/2m^{H_2})(1-X^G)/X^G$, where m is the mole fraction of the species specified.

The former relation was applied to several systems, all of which are known to belong to the case $\nu=1$. From S_b obtained by measuring the isotopic mixed potential of the hydrogen electrode in the system composed of light water and deuterium-containing hydrogen, the following S_f-values were obtained at 25°C: 3.9 for Au in 1N H_2SO_4, 4.2 for Pt and 6.2 for Ni both in 0.1 N NaOH solution.

Introduction

The isotope effect in the hydrogen electrode reaction (HER),

$$2H^+ + 2e = H_2\,,$$

is expressed in terms of the electrolytic isotope separation factor, usually that in the forward reaction (hydrogen *evolution* reaction), S_f, defined (for H-D separation) as

$$S_f \equiv \frac{V_f^H}{1-X^L}\Big/\frac{V_f^D}{X^L}\,, \qquad (1.f)$$

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where V_f^H and V_f^D are, respectively, the overall unidirectional forward rates of transfer of light hydrogen and of deuterium and X^L is the atomic fraction of deuterium in aqueous electrolyte. It has been widely accepted that S_f is characteristic of the mechanism of the HER, and hence a number of investigations have been devoted to its experimental determination[1~4] and theoretical interpretation.[5]

Only few reports are available[6,7] on the separation factor in the backward reaction (hydrogen *ionization* reaction), S_b, defined as

$$S_b \equiv \frac{V_b^H}{1-X^G} \Big/ \frac{V_b^D}{X^G}, \qquad (1.b)$$

where V_b^H and V_b^D are, respectively, the overall unidirectional backward rates of transfer of light hydrogen and of deuterium and X^G is the atomic fraction of deuterium in the hydrogen gas.

The authors have recently established[8] a reliable and convenient method of determining S_b by the observation of the isotopic mixed potential of hydrogen electrode in the system composed of solution of light water and deuterium-containing hydrogen as referred to the reversible hydrogen electrode potential in the light hydrogen system under otherwise the same conditions. Accordingly, it is desirable to establish a quantitative relation between S_f and S_b on one and the same electrode in order to derive S_f from S_b thus obtained.

We readily see from the definitions that, under the condition where the isotopic exchange equilibrium is established between hydrogen gas and aqueous solution, the ratio S_f/S_b yields the partition cefficient Q_{L-G} of deuterium, *i.e.*,

$$S_f = S_b \cdot Q_{L-G} \qquad \text{(under the exchange equilibrium)},[9] \qquad (2)$$

where Q_{L-G} is defined as

$$Q_{L-G} \equiv \left[\frac{X^L}{1-X^L} \Big/ \frac{X^G}{1-X^G} \right]_{eq.} . \qquad (3)$$

Eq. (2) does not generally apply to the case where the exchange equilibrium is not attained. However, it has been demonstrated[9] that the relation still holds under non-equilibrium conditions provided that both X^L and X^G are sufficiently small and that the hydrogen gas is equilibrated with respect to the isotopic equilibration reaction,

$$H_2 + D_2 = 2HD . \qquad (4)$$

The present paper is devoted to establish a quantitative relation between S_f and S_b which covers the whole range of X^G, while keeping X^L throughout at the natural abundance, X_o^L. This choice of X^L is made since S_f-values

treated experimentally and theoretically in the literature are usually those at low X^{L}. Based on the relation established in this work, values of S_f on several metals are obtained from S_b which is determined from the isotopic mixed potential.[8]

Theoretical

We consider the test electrode T in the system composed of a "light" water solution (containing deuterium of the natural abundance) and hydrogen gas which contains an arbitrary amount of deuterium (Fig. 1, a). For this

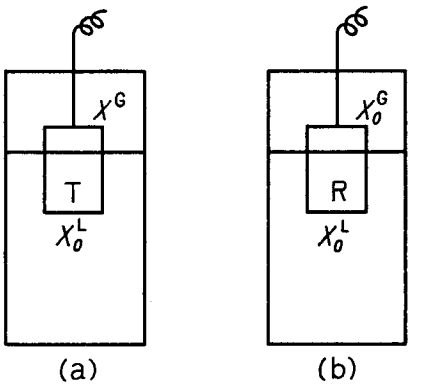

Fig. 1. (a) Test hydrogen electrode at rest in the system composed of "light" water (containing deuterium of the natural abundance, deuterium atomic fraction X_o^L) and deuterium-containing hydrogen gas (deuterium atomic fraction X^G). (b) Reversible hydrogen electrode in the "light" hydrogen system (deuterium atomic fractions X_o^L and X_o^G)

system, Eq. (1.f) is specialized as

$$S_{f,o} = \frac{V_f^H}{1-X_o^L} \Big/ \frac{V_f^D}{X_o^L}, \tag{5}$$

or using $Q_{L-G,o}$, the value of Q_{L-G} at $X^L = X_o^L$ and $X^G = X_o^G$, *i.e.*

$$Q_{L-G,o} = \left[\frac{X_o^L}{1-X_o^L} \Big/ \frac{X_o^G}{1-X_o^G} \right]_{eq.}, \tag{6}$$

as

$$S_{f,o} = Q_{L-G,o} \cdot \frac{X_o^G}{1-X_o^G} \cdot \frac{V_f^H}{V_f^D}. \tag{7}$$

The last factor in Eq. (7) has to be treated separately according as the stoichiometric number ν of the rate-determining step of the HER equals 1

and 2, respectively.[8] It is premised in the present treatment that the hydrogen isotope is transferred from the gas phase to the solution or in its reverse direction always through the rate-determining step of the HER.*)

(A) Case $\nu = 1$

From the premise stated above, it follows that two hydrogen nuclei are necessarily involved in the rate-determining step in this case.**) A typical example of this case is the so-called catalytic mechanism, *i.e.*,

$$H^+ + e \rightleftharpoons H(a), \quad 2H(a) \rightarrow H_2,$$

with the latter step determining the rate, where H(a) represents chemisorbed hydrogen atom on the electrode. Eq. (7) is rewritten in this case as

$$S_{f,o} = Q_{L-G,o} \cdot \frac{X_o^G}{1-X_o^G} \cdot \frac{2v_f^{H_2} + v_f^{HD}}{2v_f^{D_2} + v_f^{HD}}, \tag{8}$$

where $v_f^{H_2}$ etc. are the unidirectional forward rate of transfer by the rate-determining step of H_2 etc.

Here, $v_f^{H_2}$ is related to the backward rate $v_b^{H_2}$ and chemical potentials of the relevant species as[10]

$$v_f^{H_2}/v_b^{H_2} = \exp\left[(2\mu^{H(a)} - \mu^{H_2})/RT\right].$$

On account of the partial equilibrium of the step, $H^+ + e \rightleftharpoons H(a)$, $\mu^{H(a)}$ is equal to $\mu_o^{H^+} + \mu^e$. Hence we have

$$v_f^{H_2}/v_b^{H_2} = \exp\left[(2\mu_o^{H^+} + 2\mu^e - \mu^{H_2})/RT\right], \tag{9. H_2}$$

where the subscript, o, signifies the quantity in "light" water. Similarly we have, respectively, for HD and D_2,

$$v_f^{HD}/v_b^{HD} = \exp\left[(\mu_o^{H^+} + \mu_o^{D^+} + 2\mu^e - \mu^{HD})/RT\right] \tag{9. HD}$$

and

$$v_f^{D_2}/v_b^{D_2} = \exp\left[(2\mu_o^{D^+} + 2\mu^e - \mu^{D_2})/RT\right]. \tag{9. D_2}***)$$

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*) This is experimentally found to be always the case;[8] if this condition is not satisfied, no relation can be found between S_f and S_b.

**) In the mechanism, $H^+ + e \rightarrow H(a)$, $H(a) + H^+ + e \rightleftharpoons H_2$, which belongs to the case $\nu = 1$, only one hydrogen nucleus is involved in the rate-determining step. In this case, however, hydrogen can be transferred from gas phase to the solution and in its reverse direction without passing through the rate-determining step.

***) Eq. (9) is also found in the case of the so-called electrochemical mechanism:

$$H^+ + e \rightleftharpoons H(a), \qquad H(a) + H^+ + e \rightarrow H_2.$$

Further, the following relations hold for the reversible hydrogen electrode (where $\mu^{e}=\mu^{e}_{rev.}$) in the "light" hydrogen system under otherwise the same conditions, for the exchange equilibrium is established with regard to deuterium of the natural abundance though it is very little amount (Fig. 1, b),

$$2\mu_o^{H^+}+2\mu^{e}_{rev.}=\mu_o^{H_2}, \qquad (10.H_2)$$

$$\mu_o^{H^+}+\mu_o^{D^+}+2\mu^{e}_{rev.}=\mu_o^{HD} \qquad (10.HD)$$

and

$$2\mu_o^{D^+}+2\mu^{e}_{rev.}=\mu_o^{D_2}. \qquad (10.D_2)$$

Eliminating $v_f^{H_2}$, v_f^{HD} and $v_f^{D_2}$ from Eqs. (8) and (9) and replacing $\mu_o^{H^+}$ etc. with $\mu_o^{H_2}$ etc. by Eq. (10), we obtain

$$S_{f,o}=Q_{L-G,o}\cdot\frac{X_o^G}{1-X_o^G}\cdot\frac{2v_b^{H_2}\exp[(\mu_o^{H_2}-\mu^{H_2})/RT]+v_b^{HD}\exp[(\mu_o^{HD}-\mu^{HD})/RT]}{2v_b^{D_2}\exp[(\mu_o^{D_2}-\mu^{D_2})/RT]+v_b^{HD}\exp[(\mu_o^{HD}-\mu^{HD})/RT]}.$$

Now, μ^{H_2}, $\mu_o^{D_2}$ etc. are in turn given as

$$\mu^{H_2}=\mu_1^{H_2}+RT\ln m^{H_2}\cdot P, \qquad (11.H_2)$$

$$\mu_o^{D_2}=\mu_1^{D_2}+RT\ln m_o^{D_2}\cdot P \qquad (11.D_2)$$

etc., where $\mu_1^{H_2}$ and $\mu_1^{D_2}$ are, respectively, the standard chemical potentials of H_2 and D_2, m^{H_2} and $m_o^{D_2}$ are their mole fractions and P is the total hydrogen pressure. Substitution of μ^{H_2} etc. from these equations into the above equation for $S_{f,o}$ yields

$$S_{f,o}=Q_{L-G,o}\cdot\frac{X_o^G}{1-X_o^G}\cdot\frac{2v_b^{H_2}m_o^{H_2}/m^{H_2}+v_b^{HD}m_o^{HD}/m^{HD}}{2v_b^{D_2}m_o^{D_2}/m^{D_2}+v_b^{HD}m_o^{HD}/m^{HD}}. \qquad (12)$$

Here, we define σ_{23} and σ_{24} as

$$\sigma_{23}\equiv\frac{v_b^{H_2}}{m^{H_2}}\Big/\frac{v_b^{HD}}{m^{HD}} \quad\text{and}\quad \sigma_{24}\equiv\frac{v_b^{H_2}}{m^{H_2}}\Big/\frac{v_b^{D_2}}{m^{D_2}}, \qquad (13.HD),\ (13.D_2)$$

i.e., as the ratio of the specific rate of ionization of H_2 to that of HD and to that of D_2, respectively, these being assumed to be constant independent of the composition of the hydrogen gas. In terms of these "individual" separation factors, Eq. (12) assumes the form

$$S_{f,o}=Q_{L-G,o}\cdot\frac{X_o^G}{1-X_o^G}\cdot\frac{2m_o^{H_2}}{m_o^{HD}}\cdot\frac{\sigma_{23}+m_o^{HD}/2m_o^{H_2}}{1+(2m_o^{D_2}/m_o^{HD})(\sigma_{23}/\sigma_{24})}. \qquad (14)$$

The factor $X_o^G/(1-X_o^G)$ is well approximated as $m_o^{HD}/2m_o^{H_2}$ using the general relations,

$$1-X^G=m^{H_2}+m^{HD}/2 \quad\text{and}\quad X^G=m^{D_2}+m^{HD}/2, \qquad (15.H),\ (15.D)$$

with $m_o^{HD}/m_o^{H_2} \simeq 10^{-4}$ and $m_o^{D_2}/m_o^{HD} \simeq 10^{-4}$. Further the second term in the denominator of the last factor in Eq. (14) is extremely small as comparad with unity, and so is the second term in the numerator as compared with σ_{23} which is of the order of magnitude of unity. Hence, we have

$$S_{f,o} = Q_{L-G,o} \cdot \sigma_{23} . \tag{16}$$

This result could physically be understood in the following way. Under the condition that the exchange equilibrium is established in the "light" hydrogen system, we clearly have the relation (*cf.* Eq. (2))

$$S_{f,o} = Q_{L-G,o} \cdot S_{b,o} , \tag{17}$$

where $S_{b,o}$ is the value of S_b at $X^G = X_o^G$ and $X^L = X_o^L$. In the present case of $\nu = 1$, S_b is given from Eqs. (1.*b*) and (15) as

$$S_b = \frac{2v_b^{H_2} + v_b^{HD}}{2v_b^{D_2} + v_b^{HD}} \cdot \frac{2m^{D_2} + m^{HD}}{2m^{H_2} + m^{HD}} , \tag{18}$$

or in terms of σ_{23} and σ_{24} as

$$S_b = \frac{1 + \sigma_{23}(2m^{H_2}/m^{HD})}{1 + (\sigma_{23}/\sigma_{24})(2m^{D_2}/m^{HD})} \cdot \frac{2m^{D_2} + m^{HD}}{2m^{H_2} + m^{HD}} . \tag{19}$$

Consequently, S_b may depend on the isotopic composition of the hydrogen gas.*) As the "light" hydrogen gas now concerned is in equilibrium of reaction (4), we readily see that $S_{b,o}$ is practically identical with σ_{23}, that is, we have Eq. (16) above. Even if we replace the hydrogen gas with hydrogen of any isotopic composition, it would cause no variation of $S_{f,o}$ (nor of σ_{23} as assumed), that is, Eq. (16) is applicable in the whole range of X^G.

The last task of evaluating $S_{f,o}$ is therefore the evaluation of σ_{23}. As stated above σ_{23} is determinable from a single measurement of S_b using an isotopically equilibrated hydrogen gas of sufficiently small X^G. If we use hydrogen of moderate or high X^G, two values of S_b at different isotopic compositions are required in the evaluation of σ_{23} (and of σ_{24} simultaneously) by Eq. (19).

(B) Case $\nu = 2$

A typical example of this case is the so-called slow-discharge mechanism, *i.e.*,

$$H^+ + e \rightarrow H(a) , \quad 2H(a) \rightleftharpoons H_2 ,$$

with the former step determining the rate. In the present case the hydrogen

*) If the hydrogen gas is composed of H_2 and D_2 only, it follows from Eq. (19) that S_b equals σ_{24} as it should be.

gas is necessarily equilibrated isotopically through the latter step which is premised to be in partial equilibrium.

The ratio V_f^H/V_f^D in Eq. (7) is given by the ratio of the forward rates of the rate-determining (discharge) step, *i.e.*,

$$V_f^H/V_f^D = v_f^H/v_f^D . \tag{20.f}$$

Similarly we have

$$V_b^H/V_b^D = v_b^H/v_b^D . \tag{20.b}$$

As in the preceding case, v_f^H is given as[10]

$$v_f^H/v_b^H = \exp\left[(\mu_o^{H^+} + \mu^e - \mu^{H(a)})/RT\right] ,$$

or on account of the partial equilibrium of the step, $2H(a) \rightleftarrows H_2$, as

$$v_f^H/v_b^H = \exp\left[(2\mu_o^{H^+} + 2\mu^e - \mu^{H_2})/2RT\right] . \tag{21.H}$$

Similarly, we have for deuterium

$$v_f^D/v_b^D = \exp\left[(2\mu_o^{D^+} + 2\mu^e - \mu^{D_2})/2RT\right] . \tag{21.D}$$

Hence, we have from Eqs. (1.*b*), (7), (20) and (21)

$$S_{f,o} = Q_{L-G,o} \cdot S_b \cdot \frac{1-X^G}{X^G} \cdot \frac{X_o^G}{1-X_o^G} \exp\left[(2\mu_o^{H^+} - 2\mu_o^{D^+} - \mu^{H_2} + \mu^{D_2})/2RT\right] , \tag{22}$$

or, using Eqs. (10) and (11) and approximating $X_o^G/(1-X_o^G)$ as $m_o^{HD}/2m_o^{H_2}$ as above,

$$S_{f,o} = Q_{L-G,o} \cdot S_b \cdot \frac{1-X^G}{X^G} \cdot \frac{m^{HD}}{2m^{H_2}} \sqrt{\frac{(m_o^{HD})^2}{m_o^{H_2} m_o^{D_2}} \cdot \frac{m^{H_2} m^{D_2}}{(m^{HD})^2}} . \tag{23}$$

This is reduced to

$$S_{f,o} = Q_{L-G,o} \cdot S_b \cdot Z , \tag{24}$$

where

$$Z \equiv \frac{1-X^G}{X^G} \cdot \frac{m^{HD}}{2m^{H_2}} = \frac{2m^{H_2} + m^{HD}}{2m^{D_2} + m^{HD}} \cdot \frac{m^{HD}}{2m^{H_2}} \tag{25}$$

because, as stated above, the hydorgen gas over the electrode T is now always in equilibrium with respect to the reaction (4), *i.e.*, the square root term in Eq. (23) is unity. Thus, the value of $S_{f,o}$ is determinable from S_b and the composition of hydrogen gas used in the measurement of S_b.

Eqs. (24) and (25) indicate that S_b changes with X^G, for $Q_{L-G,o}$ is constant

and $S_{f,o}$ does not depend on X^G. It is clear from Eq. (25) that, since the hydrogen is equilibrated, the factor Z takes the value of unity at $X^G \simeq 0$, decreases with increase of X^G as long as $K<4$*) and reaches $K/4$ at $X^G \simeq 1$, *i.e.*,

$$S_{f,o} = Q_{L-G,o} \cdot S_{b,o} \qquad (\text{at } X^G \simeq 0) \tag{26}$$

and

$$S_{f,o} = Q_{L-G,o} \cdot S_b \cdot K/4 \qquad (\text{at } X^G \simeq 1), \tag{27}$$

where K, the equilibrium constant of the reaction (4), is to be taken at the experimental temperature. It follows that S_b increases from $S_{b,o}$ to $S_{b,o} \cdot (4/K)$ as X^G increases from zero to unity.

This variation of S_b with X^G can be visualized as follows (in terms of the present example of the slow-discharge mechanism). We define σ_{12} as the relative specific rate of ionization of H(a) to that of D(a), *i.e.*,

$$\sigma_{12} \equiv \frac{v_b^H}{1-X^A} \Big/ \frac{v_b^D}{X^A}, \tag{28}$$

and assume it to be constant independent of X^A, the atomic fraction of deuterium in the adsorbed hydrogen atoms. Then, S_b in Eq. (1. *b*) is expressed in terms of σ_{12} using Eqs. (20) and (28) as

$$S_b = \sigma_{12} \cdot \frac{X^G}{1-X^G} \cdot \frac{1-X^A}{X^A}. \tag{29}$$

Substituting this into Eq. (24), we have

$$S_{f,o} = Q_{L-G,o} \cdot \sigma_{12} \cdot Z/Q_{A-G}, \tag{30}$$

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*) Using Eq. (15), Z is expressed as

$$Z = m^{HD}(1-X^G)/X^G(2-2X^G-m^{HD}). \tag{i}$$

Differentiating Z with X^G, we have

$$\frac{dZ}{dX^G} = \frac{(m^{HD})^2-2(1-X^G)^2(m^{HD}-X^G \cdot dm^{HD}/dX^G)}{(X^G)^2(2-2X^G-m^{HD})^2}. \tag{ii}$$

Here, m^{HD} is given from Eqs. (15) and $K=(m^{HD})^2/m^{H_2}\, m^{D_2}$ as

$$m^{HD} = \left[\sqrt{1+4(4-K)(1-X^G)X^G/K} - 1\right] K/(4-K) \tag{iii}$$

(if $K=4$, $m^{HD}=2X^G[1-X^G]$). From Eqs. (ii) and (iii), we have

$$\frac{dZ}{dX^G} = -\frac{8(1-X^G)^2[1+2(4-K)(1-X^G)/K-Y]}{Y(Y+1)^2(2-2X^G-m^{HD})^2},$$

where

$$Y \equiv \sqrt{1+4(4-K)(1-X^G)X^G/K}.$$

dZ/dX^G is shown to be always negative as long as $K<4$.

where Q_{A-G} is the partition coefficient of deuterium between adsorbed hydrogen and hydrogen gas, defined as

$$Q_{A-G} \equiv \left[\frac{X^A}{1-X^A} \Big/ \frac{X^G}{1-X^G}\right]_{eq.} \tag{31}$$

Similarly, we have from Eq. (26)

$$S_{f,o} = Q_{L-G,o} \cdot \sigma_{12}/Q_{A-G,o} \qquad (\text{at } X^G \simeq 0) \tag{32}$$

where $Q_{A-G,o}$ is the value of Q_{A-G} at $X^G = X^G_o$ and $X^A = X^A_o$. Consequently, from Eqs. (30) and (32), we obtain

$$Q_{A-G}/Q_{A-G,o} = Z, \tag{33}*)$$

i.e., as seen above, the ratio decreases as X^G increases as long as $K<4$, or according to Eq. (31), X^A does not increase as rapidly as X^G increases. It follows from Eq. (29) that S_b increases with increase of X^G.

Results of preliminary experiments

Consider the cell set up by connecting solutions of the two half-cells in Fig. 1. The rest potential of the electrode T deviates from that of the reversible hydrogen electrode in the same solution due to the isotope effect in the HER. It has been demonstrated[8] that, in the case $\nu = 1$ and when the deuterium-containing hydrogen is equilibrated with respect to the reaction (4), the magnitude of the deviation E_r (isotopic mixed potential) is related with a sufficient approximation to S_b and X^G as

$$\exp(-FE_r/RT) = 1 - X^G + X^G/S_b, \tag{34}$$

and hence S_b is obtained by measuring E_r at a given X^G.

Experiments**) have been carried out at 25°C on several systems, all of which are known[7,13,14] to belong to the case $\nu = 1$, using deuterium ($X^G = 0.997$) and hydrogen-deuterium mixture ($X^G \simeq 0.5$) gases which were preliminarily equilibrated on a Pt catalyst heated at about 300°C. Combining two S_b-values

*) This relation is not necessarily based on the assumption of the slow-discharge mechanism, but on the adsorption equilibrium of hydrogen. Incidentally, even if we take the *absorbed* state of hydrogen atom in a metal instead of the *adsorbed* state, we can readily obtain exactly the same form as Eq. (33), *i.e.*,

$$Q_{M-G}/Q_{M-G,o} = Z, \tag{i}$$

where Q_{M-G} is the partition coefficient of deuterium between *absorbed* hydrogen and hydrogen gas defined in analogous form as Eq. (31). This relation has previously been implied in a treatment by STACKELBERG.[11]

**) Details of the experiment will be published elsewhere.[12]

TABLE 1. Results on relative specific rate of ionization of H_2 to that of HD (σ_{23}) and to that of D_2 (σ_{24}) and deuterium separation factor in the hydrogen evolution reaction from "light" water ($S_{f,o}$), all being near the reversible hydrogen electrode potential. In the last column are given the literature values ($S_{f,\mathrm{lit.}}$) observed under cathodic polarization (overpotential is indicated in the parenthesis)

Electrode metal	Solution	σ_{23}	σ_{24}	$S_{f,o}$	$S_{f,\mathrm{lit.}}$
Ni	0.1N NaOH	1.6 ±0.1	2.7 ±0.2	6.2	6.7 (0.35 V)[1]
Pt	0.1N NaOH	1.07±0.03	1.15±0.03	4.15	3~4 (<0.1 V)[2] in 1N H_2SO_4
Au	1N H_2SO_4	1.0 ±0.03	1.25±0.03	3.87	6.4 (0.35 V)[1]

thus obtained, both σ_{23} and σ_{24} were evaluated by Eq. (19). These values and $S_{f,o}$ (all near the reversible hydrogen electrode potential) evaluated by Eq. (16) using $Q_{\mathrm{L-G},o}=3.87$[11,15] are given in Table 1; in the last column $S_{f,\mathrm{lit.}}$, the literature values obtained by direct electrolysis, are listed for comparison.

The $S_{f,o}$-value on Ni agrees well with $S_{f,\mathrm{lit.}}$ obtained under a highly cathodic polarization. On Pt, $S_{f,o}$-value obtained in an alkaline solution agrees with $S_{f,\mathrm{lit.}}$ which was obtained[2] near the reversible potential (cathodic overpotential<0.1 V) in an acidic solution (1N H_2SO_4). Since S_f-value obtained under a highly cathodic polarization is about 7 in alkaline solution,[3] it follows that S_f in alkaline solution changes with overpotential as was found in an acidic solution.[2] A similar dependence of S_f on overpotential is also expected for Au in acidic solution, where $S_{f,o}$ is much smaller than $S_{f,\mathrm{lit.}}$ obtained under a cathodic polarization.

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