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A RELATION BETWEEN FORWARD
AND BACKWARD ISOTOPE SEPARATION FACTORS
OF THE HYDROGEN ELECTRODE REACTION :
THE DISCHARGE-COMBINATION ROUTE
# UNDER COUPLED CONTROL

By

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Abstract

A relationship is derived between the ratio of the forward electrolytic separation factor of hydrogen isotopes in the hydrogen electrode reaction to the backward one and the equilibrium partition coefficient of the isotopes between gaseous hydrogen and aqueous solution. The analysis was made for the case that the reaction takes place through the discharge-combination route with no unique rate-determining step. The relation under irreversible electrolysis is also discussed. Examples of application of the relation to experimental data are presented.

I. Introduction

The deuterium (or tritium) separation factors in the forward (anodic) and reverse uni-directional rates of the hydrogen electrode reaction (*her*)

$$H_2 + 2B = 2H^+B + 2e$$
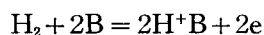
are defined by

$$S_+ = \frac{U_+^d}{1-X} \Big/ \frac{U_+^D}{X} \tag{1}$$

and

$$S_- = \frac{U_-^H}{1-Z} \Big/ \frac{U_-^D}{Z}, \tag{2}$$

where $B = H_2O$ or OH^-, X and Z are, respectively, the deuterium atomic fraction in the gaseous hydrogen and aqueous solution, U_+^H and U_+^D are partial uni-directional rates (number of atoms transferred per unit time) due

to H(protium) and D(deuterium) in the forward direction, and U^H_- and U^D_- are those in the reverse direction. Under exchange equilibrium of isotopes between gaseous and solution phases, evidently

$$U^H_+ = U^H_- \text{ and } U^D_+ = U^D_-$$

Accordingly, from Eqs. (1) and (2),

$$\left(\frac{S_+}{S_-}\right)_{eq} = \left(\frac{X}{1-X} \Big/ \frac{Z}{1-Z}\right)_{eq} = \frac{1}{Q_{lg}}, \qquad (3)$$

where Q_{lg} is the partition coefficient of the isotopes between the two phases, which is generally composition-dependent.

The relation between Q_{lg} and the separation factors under non-equilibrium condition (with respect to isotope distribution) was analyzed by HORIUTI and FUKUDA[1]. They have shown that the relation

$$(S_+/S_-)_{X,Z \simeq 0} = (1/Q_{lg})_{X,Z \simeq 0} \qquad (4)$$

holds even under non-equilibrium condition, provided that the hydrogen gas and solution phase are sufficiently dilute in deuterium and that there exists a unique rate-determining step (rds). Later the relation was investigated by YOKOYAMA and ENYO[2] in the system with arbitrary deuterium concentration in the gaseous hydrogen and sufficiently dilute heavy water ($Z \simeq 0$). The analysis was again made for the case with a unique rds.

On the other hand, some recent investigations[3] by a tracer technique indicated that the her on various metals, e.g., Pt, Rh, Ni, Au, and Ag, involves no overwhelming unique rds. This work is thus devoted to investigate the relation for the case with no unique rds, hence including the case of the coupled control. The relation is at first derived for the non-polarized condition and then its applicability under irreversible electrolysis is investigated.

II. Rates and Separation Factors of the Constituent Steps

The discharge-combination route

$$H_2 \underset{\text{step 1}}{\overset{}{\rightleftharpoons}} 2H(a), \qquad H(a) + B \underset{\text{step 2}}{\overset{}{\rightleftharpoons}} H^+B + e$$
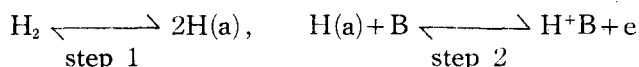
of the her has been concluded on various catalytically active metals at the reversible potential[3] and under anodic and cathodic polarizations[4,*]. The

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*) Step 2 does not necessarily represent a simple charge-transfer step; it may represent any processes involved in the transformation between H(a) and H⁺B.

forward and backward rates of step 1 (step 2) counted in number of times of occurrence per unit time will be denoted by v_{+1} and v_{-1} (v_{+2} and v_{-2}), respectively, or in number of hydrogen atoms transferred per unit time by u_{+1} and u_{-1} (u_{+2} and u_{-2}).

Deuterium separation factors of the individual steps are defined in analogous forms with Eqs. (1) and (2) as,

$$s_{+1} = \frac{u_{+1}^{\mathrm{H}}}{1-X} \bigg/ \frac{u_{+1}^{\mathrm{D}}}{X} = \frac{2v_{+1}^{\mathrm{H_2}}+v_{+1}^{\mathrm{HD}}}{1-X} \bigg/ \frac{2v_{+1}^{\mathrm{D_2}}+v_{+1}^{\mathrm{HD}}}{X} \,, \qquad (5)$$

$$s_{-1} = \frac{u_{-1}^{\mathrm{H}}}{1-Y} \bigg/ \frac{u_{-1}^{\mathrm{D}}}{Y} = \frac{2v_{-1}^{\mathrm{H_2}}+v_{-1}^{\mathrm{HD}}}{1-Y} \bigg/ \frac{2v_{-1}^{\mathrm{D_2}}+v_{-1}^{\mathrm{HD}}}{Y} \,, \qquad (6)$$

$$s_{+2} = \frac{u_{+2}^{\mathrm{H}}}{1-Y} \bigg/ \frac{u_{+2}^{\mathrm{D}}}{Y} = \frac{v_{+2}^{\mathrm{H}}}{1-Y} \bigg/ \frac{v_{+2}^{\mathrm{D}}}{Y} \,, \qquad (7)$$

and

$$s_{-2} = \frac{u_{-2}^{\mathrm{H}}}{1-Z} \bigg/ \frac{u_{-2}^{\mathrm{D}}}{Z} = \frac{v_{-2}^{\mathrm{H}}}{1-Z} \bigg/ \frac{v_{-2}^{\mathrm{D}}}{Z} \,, \qquad (8)$$

where Y is the atomic fraction of deuterium in the hydrogen adatoms. We further define the separation factors for HD and D_2 molecules which are involved in step 1.

$$\sigma_{+23} = \frac{v_{+1}^{\mathrm{H_2}}}{X^{\mathrm{H_2}}} \bigg/ \frac{v_{+1}^{\mathrm{HD}}}{X^{\mathrm{HD}}} \,, \qquad \sigma_{+24} = \frac{v_{+1}^{\mathrm{H_2}}}{X^{\mathrm{H_2}}} \bigg/ \frac{v_{+1}^{\mathrm{D_2}}}{X^{\mathrm{D_2}}} \,, \qquad (9, 10)$$

$$\sigma_{-23} = \frac{v_{-1}^{\mathrm{H_2}}}{(1-Y)^2} \bigg/ \frac{v_{-1}^{\mathrm{HD}}}{2Y(1-Y,)} \,, \qquad \sigma_{-24} = \frac{v_{-1}^{\mathrm{H_2}}}{(1-Y)^2} \bigg/ \frac{v_{-1}^{\mathrm{D_2}}}{Y^2} \,, \qquad (11, 12)$$

where $X^{\mathrm{H_2}}$ *etc.* denote mole fraction of H_2 *etc.* We will assume in the following analysis the σ's to be composition- and potential-independent as they are each concerned on a single pair of isotope molecules, but not s_{+1} and s_{-1} to be so as they involve greater numbers. Similarly, we will assume s_{+2} and s_{-2} to be independent of Y. However, we will not assume these to be independent of Z as Brönsted base involved in step 2 has different isotopic composition for different Z-values and should provide different reaction environment for step 2[*].

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[*] s_{+1} is composition-dependent since it involves X in a complex form, see Eq. (22) below. Similarly, s_{-1} is composition- and potential-dependent as Y in Eq. (25) below depends upon X (and Z) and various step rates. Consequently, S_{+} and S_{-} which involve X, Y, and various individual separation factors are generally composition- and potential-dependent.

III. Relations among various Separation Factors

Under the exchange equilibrium between the gaseous and solution phases, the following relations must be satisfied at any deuterium concentration in the system,

$$v_{+1}^{H_2} = v_{-1}^{H_2}, \quad v_{+1}^{HD} = v_{-1}^{HD}, \quad \text{and} \quad v_{+1}^{D_2} = v_{-1}^{D_2} \tag{13}$$

Employing Eqs. (9)–(12), we find

$$\frac{\sigma_{+23}^2}{\sigma_{+24}} \frac{\sigma_{-24}}{\sigma_{-23}^2} = \frac{K}{4}, \tag{14}$$

where K is the equilibrium constant of the isotopic equilibration reaction in gaseous hydrogen,

$$H_2 + D_2 = 2HD. \tag{15}$$

Substituting Eqs. (9) and (10) into Eq. (5), we obtain

$$s_{+1} = \frac{2\sigma_{+23} + X^{HD}/X^{H_2}}{\dfrac{2\sigma_{+23}}{\sigma_{+24}} \dfrac{X^{D_2}}{X^{H_2}} + \dfrac{X^{HD}}{X^{H_2}}} \frac{X}{1-X}. \tag{16}$$

We define the degree of equilibration, ρ, of the isotopic equilibration reaction (15) among hydrogen isotopes,

$$\rho \equiv X^{HD}/(X^{HD})_{eq, K=4}, \tag{17}$$

where $(X^{HD})_{eq, K=4}$ is the equilibrium mole fraction of HD under random distribution of hydrogen isotopes, viz.,

$$(X^{HD})_{eq, K=4} = 2X(1-X). \tag{18}$$

Mole fractions of the hydrogen isotopes are then expressed as[5],

and

$$\left.\begin{aligned} X^{H_2} &= (1-X)(1-\rho X), \\ X^{HD} &= 2\rho X(1-X), \\ X^{D_2} &= X(1-\rho+\rho X), \end{aligned}\right\} \tag{19}$$

and ρ is given by

$$\rho = \frac{K'}{4-K'} \left\{ \sqrt{1 + 4\frac{4-K'}{K'} X(1-X)} - 1 \right\} \Big/ 2X(1-X), \tag{20}$$

where

$$K' = (X^{HD})^2 / X^{H_2} X^{D_2} \tag{21}$$

which equals equilibrium constant K if the gas is in equilibrium of reaction (15). Equation (16) is now rewritten as,

$$s_{+1} = \frac{\sigma_{+23} - (\sigma_{+23} - 1)\, \rho X}{\dfrac{\sigma_{+23}}{\sigma_{+24}} + \left(1 - \dfrac{\sigma_{+23}}{\sigma_{+24}}\right)\rho(1-X)} \; . \tag{22*)}$$

Analogously, we obtain

$$s_{-1} = \frac{\sigma_{-23} - (\sigma_{-23} - 1)\, Y}{1 - (1 - \sigma_{-23}/\sigma_{-24})\, Y} \; . \tag{25}$$

The relation between X and Y will be discussed later, Eqs. (39) and (45). Although the σ's are assumed to be constant, s_{+1} is generally composition-dependent through X in Eq. (22), and s_{-1} is composition- and overpotential-dependent through Y in Eq. (25).

It can be shown[6] that the overall separation factors in the discharge-combination route are related to those of the constituent steps by

$$\frac{S_+}{S_-} = \frac{s_{+1}}{s_{-1}} \frac{s_{+2}}{s_{-2}} \; . \tag{26}$$

Substituting Eqs. (22) and (25) into Eq. (26), we obtain,

$$\frac{S_+}{S_-} = \frac{\sigma_{+23} - (\sigma_{+23} - 1)\, \rho X}{\dfrac{\sigma_{+23}}{\sigma_{+24}} + \left(1 - \dfrac{\sigma_{+23}}{\sigma_{+24}}\right)\rho(1-X)} \; \frac{1 - (1 - \sigma_{-23}/\sigma_{-24})\, Y}{\sigma_{-23} - (\sigma_{-23} - 1)\, Y} \; \frac{s_{+2}}{s_{-2}} \; . \tag{27}$$

(A) $X \simeq Z \simeq 0$

In the case $X \simeq 0$, $Z \simeq 0$ (hence $Y \simeq 0$) and $K' \neq 0$, Eq. (27) assumes a simpler form

$$\left(\frac{S_+}{S_-}\right)_{X, Y \simeq 0} = \frac{\sigma_{+23}}{\sigma_{-23}}\left(\frac{s_{+2}}{s_{-2}}\right)_{X, Z \simeq 0} \; . \tag{28}$$

Since σ_{+23} and σ_{-23} are assumed to be composition-independent, the right hand side (rhs) of Eq. (28), and hence its lhs, should be kept constant even in case that the system is brought to equilibrium of the isotope exchange reaction between the two phases. Accordingly, from Eq. (3),

$$\left(\frac{\sigma_{+23}}{\sigma_{-23}} \frac{s_{+2}}{s_{-2}}\right)_{X, Z \simeq 0} = \frac{1}{(Q_{lg})_{X, Z \simeq 0}} \; . \tag{29}$$

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*) If the deuterium gas is very dilute $(X \simeq 0)$ and at least partially equilibrated $(K' \neq 0)$ with respect to reaction (15), we readily see from Eq. (20), $\rho = 1$. Hence, from Eq. (22)

$$(s_{+1})_{X \simeq 0} = \sigma_{+23} \; . \qquad (K' \neq 0) \tag{23}$$

Similarly, if $X \simeq 1$ at which again $\rho = 1$ from Eq. (20) with $K' \neq 0$,

$$(s_{+1})_{X \simeq 1} = \sigma_{+24}/\sigma_{+23} \; . \qquad (K' \neq 0) \tag{24}$$

Equation (4) is thus proved for the discharge-combination route with no unique *rds*.

(B) $X \simeq 1$ and $Z \simeq 0$

Equation (29) is, however, not very useful as finite values of X and/or Z are usually required in experimental evaluation of various separation factors. One of the important cases is the combination of $X \simeq 1$ and $Z \simeq 0$; this is frequently employed in deuterium exchange experiments[3~5]. In case $X \simeq 1$ and $Z \simeq 0$, and if $K' \neq 0$ (hence $\rho = 1$), from Eq. (27),

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0} = \frac{\sigma_{+24}}{\sigma_{+23}} \frac{1-(1-\sigma_{-23}/\sigma_{-24})\,Y}{\sigma_{-23}-(\sigma_{-23}-1)\,Y} \left(\frac{s_{+2}}{s_{-2}}\right)_{X \simeq 1, Z \simeq 0}. \tag{30}$$

or, using Eq. (14),

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0} = \frac{4}{K} \frac{\sigma_{+23}}{\sigma_{-23}} \left(\frac{s_{+2}}{s_{-2}}\right)_{X \simeq 1, Z \simeq 0} \cdot A. \tag{31}$$

where

$$A \equiv \frac{\dfrac{\sigma_{-24}}{\sigma_{-23}} - \left(\dfrac{\sigma_{-24}}{\sigma_{-23}}-1\right)Y}{\sigma_{-23}-(\sigma_{-23}-1)\,Y} = 1 - \frac{1 - \dfrac{\sigma_{-24}}{\sigma_{-23}^{2}}(1-Y)}{1-\left(1-\dfrac{1}{\sigma_{-23}}\right)Y}. \tag{32}$$

As we have assumed s_{+2} and s_{-2} to be independent of Y, $(s_{+2}/s_{-2})_{X \simeq 1, Z \simeq 0} = (s_{+2}/s_{-2})_{X, Z \simeq 0}$. Hence, according to Eq. (29),

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0} = \frac{4A}{K(Q_{lg})_{X, Z \simeq 0}}. \tag{33}$$

As shown later, Eq. (45), Y in Eq. (32) can be formulated in terms of various separation factors. This means that S_+ and S_- are in principle related with each other. Nevertheless, numerical value of Y in general cannot be deduced easily and, accordingly, we will consider below special cases that Y equals unity or zero at which Eq. (32) and hence (33) assume simpler forms.

In the slow-discharge mechanism (SDM) and in case $X \simeq 1$, we may anticipate $Y \simeq 1$ and hence $A = 1$. Thus, we find

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0, \mathrm{SDM}} = \frac{4}{K(Q_{lg})_{X, Z \simeq 0}}. \tag{34}$$

This relation is in agreement with the one demonstrated elsewhere in a different way[2], *viz.*,

$$(S_-)_{X, Z \simeq 0, \mathrm{SDM}} = (S_+)_{X \simeq 1, Z \simeq 0, \mathrm{SDM}}\,(K/4)\,(Q_{lg})_{X, Z \simeq 0}, \tag{35}$$

where it may be assumed $(S_-)_{X \simeq 1, Z \simeq 0, \mathrm{SDM}} = (S_-)_{X, Z \simeq 0, \mathrm{SDM}}$ because X has nothing to do with s_{-2} which determines S_- in the slow-discharge mechanism.

Similarly, for the catalytic mechanism (CM) for which $Y \simeq Z \simeq 0$, we have, using Eq. (14),

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0, \mathrm{CM}} = \frac{\sigma_{+24}}{\sigma_{+23}^2 (Q_{lg})_{X, Z \simeq 0}}. \tag{36}$$

This relation again substantiates the one derived elsewhere[2], *viz.*,

$$(S_-)_{X, Z \simeq 0, \mathrm{CM}} = \sigma_{+23}(Q_{lg})_{X \simeq 0} \tag{37}$$

since (i), for the catalytic mechanism, $(S_+)_{X \simeq 1, Z \simeq 0, \mathrm{CM}} = (s_{+1})_{X \simeq 1, Z \simeq 0} = \sigma_{+24}/\sigma_{+23}$, *cf.* Eq. (24), and (ii), $(S_-)_{X, Z \simeq 0, \mathrm{CM}} = (S_-)_{X \simeq 1, Z \simeq 0, \mathrm{CM}}$ as $Y \simeq 0$ and X has nothing to do with s_{-1} which now determines S_-.

New factor $\sigma_{+23}^2/\sigma_{+24}$ in Eq. (36) can be evaluated directly from analysis of hydrogen isotopes ionized by anodic electrolysis (or indirectly from those cathodically evolved). Experiments have shown this to be rather close to unity: Typically, on Ni and Pd cathodes, $\sigma_{-23}^2/\sigma_{-24} = 1.1 \pm 0.1$[7], or introducing this into Eq. (14) with $K = 3.26$ at 25°C, we find $\sigma_{+23}^2/\sigma_{+24} = 0.9 \pm 0.1$.

IV. Relations under Polarization

In order to treat cases under irreversible conditions, we need a relation between X and Y so that the rhs of Eq. (27) can be evaluated. We will investigate this for the system of dilute heavy water ($Z \simeq 0$) and concentrated deuterium ($X \simeq 1$) in the gas phase. An approximate ralation would be sufficient for the present purpose, as s_{-1} becomes independent of Y when it approaches limiting values (0 and 1), *cf.* Eq. (25).

The relation should generally involve the overall affinity of the reaction since the latter determines the rates of flow of the isotopes in each steps. Nevertheless, as can be forsee qualitatively, Y approaches $X(\simeq 1)$ at high anodic overpotentials or $Z(\simeq 0)$ at high cathodic overpotentials. Thses will be demonstrated as below. Under steady-state, the total number of deuterium atoms in hydrogen adatoms is taken to be constant. Thus, with $Z \simeq 0$,

$$2v_{-1}^{\mathrm{D_2}} + v_{-1}^{\mathrm{HD}} + v_{+2}^{\mathrm{D}} = 2v_{+1}^{\mathrm{D_2}} + v_{+1}^{\mathrm{HD}} \tag{38}$$

or with Eqs. (9)~(12),

$$\frac{Y}{1-Y}\left\{\frac{1 - \left(1 - \dfrac{\sigma_{-23}}{\sigma_{-24}}\right)Y}{\sigma_{-23}(1-Y)} + \frac{r^{\mathrm{H}}}{s_{+2}}\right\} = \frac{v_{+1}^{\mathrm{H_2}}}{X^{\mathrm{H_2}} v_{-1}^{\mathrm{H_2}}}\left\{\frac{X^{\mathrm{D_2}}}{\sigma_{+24}} + \frac{X^{\mathrm{HD}}}{2\sigma_{+23}}\right\} \tag{39}$$

where the term with X^{HD} can be neglected since $X^{D_2} \gg X^{HD}$ at $X \simeq 1$ and

$$r^H \equiv v_{+2}^H / 2v_{-1}^{H_2} . \tag{40}$$

We may express $v_{-1} = v_{-1}^{H_2} + v_{-1}^{HD} + v_{-1}^{H_2}$ as

$$v_{-1} = v_{-1}^{H_2} \phi / (1-Y)^2 , \tag{41}$$

where

$$\phi \equiv (1-Y)^2 + Y \left\{ 2 - \left(2 - \frac{\sigma_{-23}}{\sigma_{-24}} \right) Y \right\} \bigg/ \sigma_{-23} . \tag{42}$$

Similarly,

$$v_{+1} = \frac{v_{+1}^{H_2}}{X^{H_2}} \left\{ X^{H_2} + \frac{X^{HD}}{\sigma_{+23}} + \frac{X^{D_2}}{\sigma_{+24}} \right\} \simeq \frac{v_{+1}^{H_2}}{\sigma_{+24}} \frac{X^{D_2}}{X^{H_2}} . \tag{43}$$

Also, defining $r \equiv v_{+2} / 2v_{-1}$, we obtain from Eqs. (7) and (41),

$$\frac{r^H (1-X)}{s_{+2}} = \frac{r\phi}{s_{+2}(1-Y) + Y} . \tag{44}$$

Eliminating $v_{+1}^{H_2} / v_{-1}^{H_2}$ and $v_{-1}^{H_2}$ from Eqs. (39), (41), and (43), and employing Eq. (44), we obtain

$$Y = \frac{(v_{+1}/v_{-1}) \phi}{\dfrac{1 + (\sigma_{-23}/\sigma_{-24} - 1) Y}{\sigma_{-23}} + \dfrac{r\phi}{s_{+2}(1-Y) + Y}} \tag{45}$$

If $r \gg 1$ (under anodic polarization, see below), Eq. (45) reduces to

$$Y = \frac{(v_{+1}/v_{-1})}{r} \left\{ s_{+2}(1-Y) + Y \right\} \tag{46}$$

Variation of r with overpotential η (in isotopically pure system) has been already discussed[8]. Although r in isotopically mixed system, which is needed, may be somewhat different from r in isotopically pure system, we will employ here the latter as we only need to know approximate behaviour or r with η.

As shown elsewhere[8], r is overpotential-dependent,

$$r = m_{eq} \exp \left\{ \left(\alpha_{+2} - \alpha_{+1} + \frac{m}{m+2} \right) f\eta \right\} , \tag{47}$$

where

$$\left. \begin{aligned} m &\equiv \Delta g_1 / \Delta g_2 , \\ m_{eq} &\equiv (\Delta g_1 / \Delta g_2)_{eq} = v_2^\circ / 2v_1^\circ , \end{aligned} \right\} \tag{48}$$

$f \equiv F/RT$, Δg_1 and Δg_2 are free energy increase of step 1 and 2, respectively, v_1° and v_2° are exchange rates of each steps, and α_{+2} and α_{+1} designate potential dependence (the transfer coefficient) of v_{+2} and v_{+1}, respectively. Numerical value of m is given by the relation[8]

$$m_{eq} \exp\left\{(\alpha_{+2}-\alpha_{+1})f\eta\right\}\left[1-\exp\left\{-\frac{2f\eta}{m+2}\right\}\right]$$
$$= \exp\left\{\frac{mf\eta}{m+2}\right\} - \exp\left\{-\frac{mf\eta}{m+2}\right\}. \tag{49}$$

The overall free energy change ΔG is related to Δg_1 and Δg_2, or to η, by

$$-\Delta G = 2F\eta = -\Delta g_1 - 2\Delta g_2. \tag{50}$$

Hence, *cf.* Eq. (48),

$$-\Delta g_1 = 2mf\eta/(m+2), \tag{51}$$

or, according to a general rate theory[9]

$$v_{+1}/v_{-1} = \exp\left\{-\Delta g_1/RT\right\} = \exp\left\{2mf\eta/(m+2)\right\}. \tag{52}$$

Anodic region

Evaluation of m from Eq. (49) and then calculation of r by Eq. (47) readily show that r is a sharp function of η, increasing with positive increase of η. Accordingly, in the region $\eta \gg RT/F$, $r \gg 1$ unless m_{eq} is extremety small. Further, with $m_{eq} \neq 0$, Eq. (49) reduces to

$$m_{eq} \exp\left\{(\alpha_{+2}-\alpha_{+1})f\eta\right\} = \exp\left\{mf\eta/(m+2)\right\}, \tag{53}$$

or, elimination of m_{eq} and η from Eqs. (47), (52), and (53) yields

$$r = v_{+1}/v_{-1}. \qquad (\eta \gg RT/F) \tag{54}$$

Therefore, from Eq. (46), we find $Y \simeq 1$, irrespective of the magnitude of s_{+2}.

Substituting $X \simeq 1$, $\rho \simeq 1$, and $Y \simeq 1$ into Eq. (27),

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0, \eta \gg RT/F} = \frac{\sigma_{+24}}{\sigma_{+23}} \frac{\sigma_{-23}}{\sigma_{-24}} \frac{s_{+2}}{s_{-2}}$$

or using Eqs. (14) and (29), finally,

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0, \eta \gg RT/F} = \frac{4}{K(Q_{lq})_{X, Z \simeq 0}}. \tag{55}$$

This enables us to evaluate S_- in the anodic region once S_+ is determined. With $K = 3.26$ at 25°C, $(S_-)_{X \simeq 1, Z \simeq 0, \eta \gg RT/F}$ calculated from $(S_+)_{X \simeq 1, Z \simeq 0, \eta \gg RT/F}$ should be *ca.* 0.8 times that given by Eq. (4).

Cathodic region

Under sufficiently large cathodic overpotentials, both v_{+1}/v_{-1} and r in Eq. (45) must be extremely small. Hence, we readily see

$$Y \simeq 0 \qquad (-\eta \gg RT/F) \tag{56}$$

Accordingly, Eq. (27) yields ($\rho = 1$ at $X \simeq 1$),

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0, -\eta \gg RT/F} = \frac{\sigma_{+24}}{\sigma_{+23}}\frac{1}{\sigma_{-23}}\frac{S_{+2}}{S_{-2}}$$

or, with Eqs. (14) and (29),

$$\left(\frac{S_+}{S_-}\right)_{X \simeq 1, Z \simeq 0, -\eta \gg RT/F} = \frac{\sigma_{+24}}{\sigma_{+23}^2(Q_{lg})_{X,Z \simeq 0}}. \tag{57}$$

in which, as obtained above, $\sigma_{+23}^2/\sigma_{+24} = 0.9 \pm 0.1^{7)}$. This indicates that the evaluation of $(S_-)_{X \simeq 1, Z \simeq 0, -\eta \gg RT/F}$ with Eq. (4) gives too large a value by *ca.* 10 percent.

V. Examples

Analysis of the isotopic mixed potential[10] on Pt which is near the reversible *her* potential yields $(S_+)_{X \simeq 1, Z \simeq 0}$ to be 1.06. As the *her* on Pt in acidic solution closely obey the catalytic mechanism[4], we may apply Eq. (36) with $\sigma_{+23}^2/\sigma_{+24} \simeq 0.9$ and $(Q_{lg})_{X, Z \simeq 0} = 3.87$ at 25°C[11,12], yielding, $(S_-)_{X \simeq 1, Z \simeq 0, \eta \simeq 0} \simeq 3.7$. In the anodic region, S_+ on Pt is very close to unity[13]. Hence, from Eq. (55), we obtain, with $K = 3.26$,

$$(S_-)_{X \simeq 1, Z \simeq 0, \eta \gg RT/F} \simeq 3.2$$

A significant variation of S_- on Pt has been reported by FUKUDA and HORIUTI[14] or by others[15,16]. These appear to indicate decrease of S_- with decreasing cathodic overpotential, approaching 3.5~3.7. The above evaluations of S_- at the reversible potential or in the anodic region provide a reasonable interpretation of the latter value. Detailed analysis of variation of S_- with overpotential will be discussed separately[6].

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