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A THEOREM ON ELECTROLYTIC SEPARATION FACTORS

By

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Summary

A theorem $S_l/S_g=S$ was demonstrated for the isotopic separation by irreversible electrolysis in the limiting case of low content of deuterium D in protium P, assuming that the mechanism underlying the electrolysis is one of the electrochemical, catalytic and slow discharge mechanisms ; $S_l\equiv(\Delta P_l/\Delta D_l)/(P_l/D_l)$ or $S_g\equiv(\Delta P_g/\Delta D_g)/(P_g/D_g)$ is the forward or the backward separation factor, where $-\Delta P_l$ or $-\Delta P_g$ is the rate of P transferred unidirectionally from aqueous electrolyte to hydrogen gas or reversely, $-\Delta D_l$ or $-\Delta D_g$ is the rate, with which D is transferred similarly unidirectionally, P_l or D_l is the amount of P or D in aqueous electrolyte and P_g or D_g is that in hydrogen gas ; S is the partition coefficient of D between aqueous electrolyte and hydrogen gas defined as the particular value $S\equiv(D_lP_g/D_gP_l)_{eq}$ of D_lP_g/D_gP_l in exchange equilibrium between them.

It was shown that the above theorem holds practically for a finite D-content in the experimental condition of the foregoing work[4], *i. e.* for 8.49% deuterium in protium, of 1.34 N H_2SO_4 over the range of hydrogen overvoltage from 0.02 to 0.55 volt under atmosphere of 12 cmHg total pressure of electrolyzed hydrogen saturated with water vapour. The theorem is shown exact, on the other hand, for any D-content, provided that the isotopic composition of hydrogen gas is that in exchange equilibrium with the aqueous electrolyte.

Introduction

One of the present authors previously advanced the equation[1]

$$S_l/S_g = S \tag{1}$$

as valid for reversible hydrogen electrode, where

$$S_l \equiv \frac{\Delta P_l}{\Delta D_l} \Big/ \frac{P_l}{D_l} \tag{2. l}$$

is the separation factor of the usual sense, $-\Delta P_l$ or $-\Delta D_l$ is the rate of protium or deuterium transferred unidirectionally from the solution to hydrogen by electrolysis, P_l or D_l is the amount of protium or deuterium to be electrolyzed in aqueous electrolyte,

$$S_g \equiv \frac{\Delta P_g}{\Delta D_g} \Big/ \frac{P_g}{D_g} \tag{2. g}$$

is, so to speak, the separation factor in the reverse direction, $-\Delta P_g$ or $-\Delta D_g$ is the unidirectional rate of protium or deuterium transferred reversely and P_g or D_g is the amount of protium or deuterium in gas. S is the partition coefficient of deuterium between aqueous electrolyte and hydrogen gas defined as the particular value $(D_l P_g / D_g P_l)_{eq}$ of $D_l P_g / D_g P_l$ in exchange equilibrium between the aqueous electrolyte and the coexisting hydrogen, *i.e.*

$$S = (D_l P_g / D_g P_l)_{eq} \tag{3. a}$$

or for a fixed value of D_l / P_l

$$S = D_l P_{g,eq} / D_{g,eq} P_l \,, \tag{3. b}$$

where the suffix *eq* signifies the particular values in the exchange equilibrium as in what follows. It is plain that (1) holds in the exchange equilibrium[1], where $\Delta P_g = \Delta P_l$ and $\Delta D_g = \Delta D_l$.

The present paper is concerned with the investigation of (1) in irreversible electrolysis both in the cases of infinitely low and finite deuterium content. The aqueous electrolyte will be simply termed solution in what follows. Protium and deuterium will be signified discriminantly by P and D or represented by H without discrimination between isotopes.

The present theorem is stated with special reference to the electrolytic separation of deuterium from protium but readily extended to any case of electrolytic separation of isotopes.

§ 1. Theorem $S_l / S_g = S$ for Infinitely Low Deuterium Content

In case of the electrochemical or the catalytic mechanism, two hydrogen nuclei are transferred from solution to hydrogen gas by every act of the rate-determining step

$$H_2^+(a) + \varepsilon \longrightarrow H_2 \tag{4. a}$$

or

$$2H(a) \longrightarrow H_2 \,, \tag{5. a}$$

which follows respectively the formation of adsorbed hydrogen molecule-ion $H_2^+(a)$, *i.e.*

$$2H^+ + \varepsilon \longrightarrow H_2^+(a) \tag{4. b}$$

or that of adsorbed hydrogen atom on the electrode H(a), *i.e.*

$$H^+ + \varepsilon \longrightarrow H(a) \,; \tag{5. b}$$

in case of the slow discharge mechanism just a single hydrogen nucleus is similarly transferred by the rate-determining step of (5.b) followed by (5.a). The number of hydrogen nuclei thus transferred by one act of the rate-determining step will be denoted by n.

The n hydrogen nuclei may consist of different isotopes. In the limiting case of low deuterium content, protons are transferred practically by the rate-determining step (P), which transfers n protons exclusively, while deuterons are similarly transferred by that (D), which transfers one deuteron along with $n-1$ protons. We have in consequence

$$\Delta P_l = n\vec{v}(\mathrm{P}), \quad \Delta P_g = n\overleftarrow{v}(\mathrm{P}), \qquad (6.\mathrm{IP}),\ (6.\mathrm{FP})$$

$$\Delta D_l = \vec{v}(\mathrm{D}) \quad \text{and} \quad \Delta D_g = \overleftarrow{v}(\mathrm{D}), \qquad (6.\mathrm{ID}),\ (6.\mathrm{FD})$$

where $\vec{v}(\mathrm{P})$ or $\overleftarrow{v}(\mathrm{P})$ is the forward or the backward rate of (P) and $\vec{v}(\mathrm{D})$ or $\overleftarrow{v}(\mathrm{D})$ is that of (D).

The forward and the backward rates of a step, *i.e.* $\vec{v}$ and $\overleftarrow{v}$ are expressed in general[2)3)], as

$$\vec{v} = \kappa kT/h \cdot p^*/p^{\mathrm{I}}, \quad \overleftarrow{v} = \kappa kT/ \cdot p^*/p^{\mathrm{F}}, \qquad (7.\vec{v}),\ (7.\overleftarrow{v})$$

where κ is the transmission coefficient and p^*, p^{I} and p^{F} are the BOLTZMANN factor of the chemical potentials respectively of the critical complex $*$, the initial complex I and the final complex F of the step. We have from (6) and (7)

$$\Delta P_l/\Delta P_g = p^{\mathrm{F(P)}}/p^{\mathrm{I(P)}}, \quad \Delta D_l/\Delta D_g = p^{\mathrm{F(D)}}/p^{\mathrm{I(D)}},$$

where $p^{\mathrm{F(P)}}$ or $p^{\mathrm{I(P)}}$ is the p^{F} or p^{I} appropriate to $\overleftarrow{v}(\mathrm{P})$ or $\vec{v}(\mathrm{P})$ and $p^{\mathrm{F(D)}}$ or $p^{\mathrm{I(D)}}$ that to $\overleftarrow{v}(\mathrm{D})$ or $\vec{v}(\mathrm{D})$ respectively. We have from (2) and the above two equations

$$\frac{S_l}{S_g} = \frac{p^{\mathrm{F(P)}}p^{\mathrm{I(D)}}}{p^{\mathrm{I(P)}}p^{\mathrm{F(D)}}} \Big/ \frac{D_g P_l}{D_l P_g}. \qquad (8)$$

The I(P), F(P), I(D) and F(D) are given by definition, as

$$\mathrm{I(P)} \equiv \mathrm{P}_2^+(\mathrm{a}) + \varepsilon, \quad \mathrm{F(P)} \equiv \mathrm{P}_2, \qquad (9.\mathrm{IP}),\ (9.\mathrm{FP})$$

$$\mathrm{I(D)} \equiv \mathrm{PD}^+(\mathrm{a}) + \varepsilon \quad \text{and} \quad \mathrm{F(D)} \equiv \mathrm{PD} \qquad (9.\mathrm{ID}),\ (9.\mathrm{FD})$$

for the electrochemical mechanism,

$$\mathrm{I(P)} \equiv 2\mathrm{P(a)}, \quad \mathrm{F(P)} \equiv \mathrm{P}_2, \qquad (10.\mathrm{IP}),\ (10.\mathrm{FP})$$

$$\mathrm{I(D)} \equiv \mathrm{P(a)} + \mathrm{D(a)} \quad \text{and} \quad \mathrm{F(D)} \equiv \mathrm{PD} \qquad (10.\mathrm{ID}),\ (10.\mathrm{FD})$$

for the catalytic mechanism and

$$\mathrm{I(P)} \equiv \mathrm{P}^+ + \varepsilon, \quad \mathrm{F(P)} \equiv \mathrm{P(a)}, \qquad (11.\mathrm{IP}),\ (11.\mathrm{FP})$$

$$\mathrm{I(D)} \equiv \mathrm{D}^+ + \varepsilon \quad \text{and} \quad \mathrm{F(D)} \equiv \mathrm{D(a)} \qquad (11.\,\mathrm{ID}),\ (11.\,\mathrm{FD})$$

for the slow discharge mechanism.

We now refer to the following relations shown generally valid[3], for developing the factor $p^{F(P)}p^{I(D)}/p^{I(P)}p^{F(D)}$ in (8). The $p^{F(P)}$ *etc.* are represented by p^{δ}, where δ stands for F(P) *etc.* If δ consists of several statistically independent parts δ_i's, *e.g.* $P_2^+(a)$ and ε as in (9. IP)[3],

$$p^{\delta} = \prod_i p^{\delta_i} \qquad (12.\,a)$$

and if two states δ_A and δ_B of δ are in equilibrium with each other[3],

$$p^{\delta_A} = p^{\delta_B}\,. \qquad (12.\,b)$$

Admitting that the steps other than the rate-determining one are respectively in equilibria, we have according to (9), (10), (11) and (12)

$$p^{I(P)} = (p^{P^+}p^{\varepsilon})^2, \quad p^{F(P)} = p^{P_2} \qquad (13.\,\mathrm{IP}),\ (13.\,\mathrm{FP})$$

$$p^{I(D)} = p^{P^+}p^{D^+}(p^{\varepsilon})^2, \quad p^{F(D)} = p^{PD} \qquad (13.\,\mathrm{ID}),\ (13.\,\mathrm{FD})$$

commonly for the electrochemical and the catalytic mechanisms, and

$$p^{I(P)} = p^{P^+}p^{\varepsilon}, \quad p^{F(P)} = p^{P_2}/p^{P(a)}, \qquad (14.\,\mathrm{IP}),\ (14.\,\mathrm{FP})$$

$$p^{I(D)} = p^{D^+}p^{\varepsilon}, \quad p^{F(D)} = p^{PD}/p^{P(a)} \qquad (14.\,\mathrm{ID}),\ (14.\,\mathrm{FD})$$

for the slow discharge mechanism. Substituting $p^{I(P)}$ *etc.* from (13) or (14) into (8), we have in any case

$$\frac{S_l}{S_g} = \frac{p^{P_2}}{p^{PD}}\,\frac{p^{D^+}}{p^{P^+}} \bigg/ \frac{D_g P_l}{D_l P_g}\,. \qquad (15)$$

The p^{P_2} or p^{PD} is now expressed as[3]

$$p^{P_2} = Q^{P_2}/N^{P_2}, \quad p^{PD} = Q^{PD}/N^{PD}, \qquad (16.\,\mathrm{P}),\ (16.\,\mathrm{D})$$

where Q^{P_2} or Q^{PD} is the partition function of a single molecule P_2 or PD in unit volume respectively, which is a function solely of temperature and N^{P_2} or N^{PD} is the concentration of P_2- or PD-molecules in gas. Noting that

$$N^{PD}/N^{P_2} = 2D_g/P_g \qquad (17)$$

in the present limiting case, we have from (15) and (16)

$$\frac{S_l}{S_g} = 2\,\frac{p^{D^+}}{p^{P^+}}\,\frac{Q^{P_2}}{Q^{PD}} \bigg/ \frac{P_l}{D_l}\,.$$

Eqs. (16) and (17) assume the particular forms in case, where the hydrogen gas is in exchange equilibrium with the solution, *i.e.*

$$p_{eq}^{P_2} = Q^{P_2}/N_{eq}^{P_2}, \quad p_{eq}^{PD} = Q^{PD}/N_{eq}^{PD} \tag{18}$$

and

$$N_{eq}^{PD}/N_{eq}^{P_2} = 2D_{g,eq}/P_{g,eq} .$$

We have now from the above four equations

$$\frac{S_l}{S_g} = \frac{p^{D^+} p_{eq}^{P_2}}{p^{P^+} p_{eq}^{PD}} \cdot \frac{D_l P_{g,eq}}{P_l D_{g,eq}} . \tag{19}$$

The first factor of the above equation is unity because of the exchange equilibrium, hence of equilibrium of the reaction,

$$D^+ + P_2 = P^+ + PD ,$$

for which

$$p^{D^+} p_{eq}^{P_2} = p^{P^+} p_{eq}^{PD} \tag{20}$$

according to (12). Hence we have (1) by (3.b).

§ 2. Slow Discharge Mechanism for Finite Deuterium Content

We now investigate the validity of the theorem (1) for finite deuterium content. In case of the slow discharge mechanism, (15) is exact even for finite deuterium content, since (6) and in consequence (8) impliy no approximation, n being unity in this case. We have from (3.b), (15) and (20), eliminating P_l/D_l and p^{D^+}/p^{P^+} from them,

$$\frac{S_l}{S_g} = f_S S , \tag{21. a}$$

where

$$f_S = \frac{p_{eq}^{PD} p^{P_2}}{p_{eq}^{P_2} p^{PD}} \frac{P_g D_{g,eq}}{D_g P_{g,eq}}$$

or according to (16)

$$f_S = \frac{N^{PD} N_{eq}^{P_2} P_g D_{g,eq}}{N^{P_2} N_{eq}^{PD} D_g P_{g,eq}} . \tag{21. b}$$

The P_g/D_g and $D_{g,eq}/P_{g,eq}$ are expressed in the general case of finite deuterium content, as

$$\frac{P_g}{D_g} = \frac{2N^{P_2} + N^{PD}}{N^{PD} + 2N^{D_2}}, \quad \frac{D_{g,eq}}{P_{g,eq}} = \frac{N_{eq}^{PD} + 2N_{eq}^{D_2}}{2N_{eq}^{P_2} + N_{eq}^{PD}}, \tag{22. a), (22. b}$$

hence according to (21.b)

$$f_S = \frac{2+N^{PD}/N^{P_2}}{1+2N^{D_2}/N^{PD}} \cdot \frac{1+2N_{eq}^{D_2}/N_{eq}^{PD}}{2+N_{eq}^{PD}/N_{eq}^{P_2}}\,, \tag{23}$$

which reduces to unity for small deuterium content, where $N^{PD}/2N^{P_2}$, $2N^{D_2}/N^{PD}$ and their equilibrium values are negligibly small compared with unity.

The f_S is calculated for the experimental condition of the foregoing paper[4], substituting the ratios N^{PD}/N^{P_2} and $N^{D_2}/N^{PD}=(N^{D_2}/N^{P_2})/(N^{PD}/N^{P_2})$ at each overvoltage η[*] respectively by $(N^{PD}/N^{P_2})_m$ and $(N^{D_2}/N^{P_2})_m/(N^{PD}/N^{P_2})_m$, where $(N^{PD}/N^{P_2})^m$ or $(N^{D_2}/N^{P_2})_m$ are the mean of the values of N^{PD}/N^{P_2} or N^{D_2}/N^{P_2} at the overvoltage as given in Table 1 of the foregoing paper[4]. The equilibrium values of N^{PD}/N^{P_2} and N^{D_2}/N^{PD} in (23) are calculated from the equilibrium constant, *i.e.*

$$K \equiv (N_{eq}^{PD})^2/N_{eq}^{P_2}N_{eq}^{D_2} \tag{24. a}$$

of the reaction $P_2+D_2=2PD$ and from the equation derived from (3.b) and (22.b),

$$S\frac{P_l}{D_l} = \frac{2N_{eq}^{P_2}+N_{eq}^{PD}}{N_{eq}^{PD}+2N_{eq}^{D_2}}\,. \tag{24. b}$$

The K is interpolated from the observations of UREY[5], as

$$K=3.23 \quad \text{at} \quad 15°\text{C}\,, \tag{25. a}$$

whereas the left-hand side of (24.b) is calculated from the atomic fraction $x_l=0.0849$[4] of deuterium in the solution and $S=4.13\pm0.04$[4] at 15°C, as

$$SP_l/D_l = 44.5\,, \qquad 15°\text{C}\,. \tag{25. b}$$

Eqs. (24) are simultaneous equations for $N_{eq}^{PD}/N_{eq}^{P_2}$ and $N_{eq}^{D_2}/N_{eq}^{PD}$, which are determined on the base of the values of (25) as shown on the top of Table 1.

TABLE 1. $f_S \equiv \dfrac{2+N^{PD}/N^{P_2}}{1+2N^{D_2}/N^{PD}} \dfrac{1+2N_{eq}^{D_2}/N_{eq}^{PD}}{2+N_{eq}^{PD}/N_{eq}^{P_2}}$

$x_l=0.0849$, $N_{eq}^{PD}/N_{eq}^{P_2}=0.0446$, $N_{eq}^{D_2}/N_{eq}^{PD}=0.0138$

Overvoltage η[*] volt	N^{PD}/N^{P_2}	N^{D_2}/N^{PD}	f_S
0.02	0.0480	0.0105	1.0081
0.03	0.0473	0.0106	1.0076
0.10	0.0382	0.0083	1.0077
0.20	0.0290	0.0057	1.0083
0.27	0.0284	0.0047	1.0100
0.39	0.0292	0.0068	1.0062
0.55	0.0300	0.0078	1.0046

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[*] The potential of the reversible hydrogen electrode minus that of the test electrode.

The f_S is now calculated by (23) at each overvoltage as shown in Table 1. We see from Table 1 that f_S differs from unity by 1.00% at most whole throughout the experimental condition, hence by (21.a) that the theorem (1) holds within errors of S-measurement under the experimental condition of the foregoing work[4] in case of the slow discharge mechanism being operative.

§ 3. Electrochemical and Catalytic Mechanism for Finite Deuterium Content

Eq. (15) is no more exact for a finite deuterium content in the case of the electrochemical and the catalytic mechanism, where $n=2$, since (6) underlying (15) is only approximate. Exactly ΔP_l *etc.* must be expressed as

$$\Delta P_l = 2\overrightarrow{v}(\mathrm{P_2})+\overrightarrow{v}(\mathrm{PD}) ,$$

$$\Delta D_l = \overrightarrow{v}(\mathrm{PD})+2\overrightarrow{v}(\mathrm{D_2}) ,$$

$$\Delta P_g = 2\overleftarrow{v}(\mathrm{P_2})+\overleftarrow{v}(\mathrm{PD}) ,$$

and

$$\Delta D_g = \overleftarrow{v}(\mathrm{PD})+2\overleftarrow{v}(\mathrm{D_2}) ,$$

where $\overrightarrow{v}(\mathrm{P_2})$, $\overrightarrow{v}(\mathrm{PD})$ and $\overrightarrow{v}(\mathrm{D_2})$ are rates of the rate-determining steps, which transfer two protons, one proton and one deuteron, and two deuterons respectively forward; $\overleftarrow{v}(\mathrm{P_2})$, $\overleftarrow{v}(\mathrm{PD})$ and $\overleftarrow{v}(\mathrm{D_2})$ are the corresponding backward rates respectively. The $\overrightarrow{v}(\mathrm{P_2})$ *etc.* are expressed in accordance with (7), assuming κ common as

$$\left.\begin{array}{ll}\overrightarrow{v}(\mathrm{P_2}) = \kappa kT/h\cdot p^{*(\mathrm{P_2})}/p^{\mathrm{I(P_2)}} , & \overleftarrow{v}(\mathrm{P_2}) = \kappa kT/h\cdot p^{*(\mathrm{P_2})}/p^{\mathrm{F(P_2)}} , \\ \overrightarrow{v}(\mathrm{PD}) = \kappa kT/h\cdot p^{*(\mathrm{PD})}/p^{\mathrm{I(PD)}} , & \overleftarrow{v}(\mathrm{PD}) = \kappa kT/h\cdot p^{*(\mathrm{PD})}/p^{\mathrm{F(PD)}} , \\ \overrightarrow{v}(\mathrm{D_2}) = \kappa kT/h\cdot p^{*(\mathrm{D_2})}/p^{\mathrm{I(D_2)}} , & \overleftarrow{v}(\mathrm{D_2}) = \kappa kT/h\cdot p^{*(\mathrm{D_2})}/p^{\mathrm{F(D_2)}} , \end{array}\right\} \quad (26)$$

where $p^{\mathrm{I(P_2)}}$ *etc.* are p^{I}'s of the rate-determining step transferring two protons *etc.*, which are expressed commonly for the electrochemical and the catalytic mechanism as in case of (13) by virtue of the equilibrium of the step other than the rate-determining one, as

$$\left.\begin{array}{ll} p^{\mathrm{I(P_2)}} = (p^{\mathrm{P^+}}p^{\varepsilon})^2 , & p^{\mathrm{F(P_2)}} = p^{\mathrm{P_2}} , \\ p^{\mathrm{I(PD)}} = p^{\mathrm{P^+}}p^{\mathrm{D^+}}(p^{\varepsilon})^2 , & p^{\mathrm{F(PD)}} = p^{\mathrm{PD}} , \\ p^{\mathrm{I(D_2)}} = (p^{\mathrm{D^+}}p^{\varepsilon})^2 , & p^{\mathrm{F(D_2)}} = p^{\mathrm{D_2}} . \end{array}\right\} \quad (27)$$

The $p^{*(\mathrm{P_2})}$, $p^{*(\mathrm{PD})}$ and $p^{*(\mathrm{D_2})}$ are the p^*'s respectively relevant to the critical complexes $*(\mathrm{P_2})$, $*(\mathrm{PD})$ and $*(\mathrm{D_2})$ of the rate-determining steps, which transfer two protons, one proton and one deuteron, and two deuterons respectively. We have from (26) and (27)

$$\left.\begin{aligned}
\varDelta P_l &= 2\vec{v}(\mathrm{P_2})+\vec{v}(\mathrm{PD}) = \kappa\frac{kT}{h}\frac{1}{(p^{\varepsilon})^2}\left\{2\frac{p^{*(\mathrm{P_2})}}{(p^{\mathrm{P^+}})^2}+\frac{p^{*(\mathrm{PD})}}{p^{\mathrm{P^+}}p^{\mathrm{D^+}}}\right\},\\
\varDelta D_l &= \vec{v}(\mathrm{PD})+2\vec{v}(\mathrm{D_2}) = \kappa\frac{kT}{h}\frac{1}{(p^{\varepsilon})^2}\left\{\frac{p^{*(\mathrm{PD})}}{p^{\mathrm{P^+}}p^{\mathrm{D^+}}}+2\frac{p^{*(\mathrm{D_2})}}{(p^{\mathrm{D^+}})^2}\right\},\\
\varDelta P_g &= 2\overleftarrow{v}(\mathrm{P_2})+\overleftarrow{v}(\mathrm{PD}) = \kappa\frac{kT}{h}\left\{2\frac{p^{*(\mathrm{P_2})}}{p^{\mathrm{P_2}}}+\frac{p^{*(\mathrm{PD})}}{p^{\mathrm{PD}}}\right\},\\
\varDelta D_g &= \overleftarrow{v}(\mathrm{PD})+2\overleftarrow{v}(\mathrm{D_2}) = \kappa\frac{kT}{h}\left\{\frac{p^{*(\mathrm{PD})}}{p^{\mathrm{PD}}}+2\frac{p^{*(\mathrm{D_2})}}{p^{\mathrm{D_2}}}\right\},
\end{aligned}\right\}\qquad(28)$$

hence according to (2)

$$\frac{S_l}{S_g}=\frac{p^{\mathrm{D^+}}}{p^{\mathrm{P^+}}}\frac{p^{\mathrm{P_2}}}{p^{\mathrm{PD}}}\frac{D_l}{P_l}\frac{P_g}{D_g}f_1f_2\,,\qquad(29.\,\mathrm{a})$$

where

$$f_1=\frac{2+p^{*(\mathrm{PD})}p^{\mathrm{P^+}}/p^{*(\mathrm{P_2})}p^{\mathrm{D^+}}}{2+p^{*(\mathrm{PD})}p^{\mathrm{P_2}}/p^{*(\mathrm{P_2})}p^{\mathrm{PD}}}\,,\qquad f_2=\frac{1+2p^{*(\mathrm{D_2})}p^{\mathrm{PD}}/p^{*(\mathrm{PD})}p^{\mathrm{D_2}}}{1+2p^{*(\mathrm{D_2})}p^{\mathrm{P^+}}/p^{*(\mathrm{PD})}p^{\mathrm{D^+}}}\,.$$

(29. b), (29. c)

The factor $p^{\mathrm{D^+}}p^{\mathrm{P_2}}D_lP_g/p^{\mathrm{P^+}}p^{\mathrm{PD}}P_lD_g$ in (29.a) is the right-hand side of (15), which is transformed into f_SS as in (21.a). Hence we have

$$S_l/S_g=fS\,,\qquad(30.\,\mathrm{a})$$

where

$$f=f_Sf_1f_2\,.\qquad(30.\,\mathrm{b})$$

The ratios $p^{*(\mathrm{PD})}/p^{*(\mathrm{P_2})}$, $p^{*(\mathrm{D_2})}/p^{*(\mathrm{PD})}$, $p^{\mathrm{P^+}}/p^{\mathrm{D^+}}$, $p^{\mathrm{P_2}}/p^{\mathrm{PD}}$ and $p^{\mathrm{PD}}/p^{\mathrm{D_2}}$ comprized in (29.b) and (29.c) are now evaluated in the subsequent sections.

§ 4. Evaluation of $p^{*(\mathrm{PD})}/p^{*(\mathrm{P_2})}$ and $p^{*(\mathrm{D_2})}/p^{*(\mathrm{PD})}$

The ratios $p^{*(\mathrm{PD})}/p^{*(\mathrm{P_2})}$ and $p^{*(\mathrm{D_2})}/p^{*(\mathrm{PD})}$ are evaluated for the electrochemical and the catalytic mechanism as follows. We have, according to the general theory of reaction rate[2)3)],

$$p^{*(\mathrm{P_2})}=G^*\Theta_{\sigma^*(0)}q_0^{*(\mathrm{P_2})}\exp\left(-\varepsilon_0^*/kT\right)$$

both for the electrochemical and the catalytic mechanism, where G^* is the number of sites σ^*'s for the critical complex on the surface of the electrode, $\Theta_{\sigma^*(0)}$ is the probability of site σ^* being unoccupied, ε_0^* the minimum potential energy of the critical complex, which is admitted to be constant irrespective of isotopic replacement in extension of the implicit postulate of UREY and RITTENBERG[6)] and $q_0^{*(\mathrm{P_2})}$ is the BOLTZMANN factor of the reversible work[3)] required for bringing the critical complex $*(P_2)$ from the standard states of its constituents onto a definite, preliminarily evacuated site σ^*. Since $G^*\Theta_{\sigma^*(0)}$ and ε_0^* are respectively common for one and the same electrode at a definite condition, we have for the two ratios in question

$$p^{*(PD)}/p^{*(P_2)} = q_0^{*(PD)}/q_0^{*(P_2)}, \quad p^{*(D_2)}/p^{*(PD)} = q_0^{*(D_2)}/q_0^{*(PD)}, \qquad (31.\text{a}),\ (31.\text{b})$$

where $q_0^{*(PD)}$ or $q_0^{*(D_2)}$ is the quantity similar to $q_0^{*(P_2)}$ respectively appropriate to the critical complex $*(PD)$ or $*(D_2)$.

The $q_0^{*(P_2)}$, $q_0^{*(PD)}$ and $q_0^{*(D_2)}$ were worked out for the electrochemical mechanism, as[7)]

$$q_0^{*(P_2)} = \frac{\sqrt{2\pi I^*(P_2)kT}}{2h} \cdot \prod_{j=1}^{4}\left[1-\exp\left\{-h\nu_j^*(P_2)/kT\right\}\right]^{-1} \cdot \exp\left\{-h\sum_{j=1}^{4}\nu_j^*(P_2)/2kT\right\}, \qquad (32.\ P_2)$$

$$q_0^{*(PD)} = \frac{\sqrt{2\pi I^*(PD)kT}}{h} \cdot \prod_{j=1}^{4}\left[1-\exp\left\{-h\nu_j^*(PD)/kT\right\}\right]^{-1} \cdot \exp\left\{-h\sum_{j=1}^{4}\nu_j^*(PD)/2kT\right\}, \qquad (32.\ PD)$$

and

$$q_0^{*(D_2)} = \frac{\sqrt{2\pi I^*(D_2)kT}}{2h} \cdot \prod_{j=1}^{4}\left[1-\exp\left\{-h\nu_j^*(D_2)/kT\right\}\right]^{-1} \cdot \exp\left\{-h\sum_{j=1}^{4}\nu_j^*(D_2)/2kT\right\}, \qquad (32.\ D_2)$$

where $I^*(P_2)$ *etc.* are the moments of inertia of rotation of the critical complexes

TABLE 2. Constants of Critical Complex of the Rate-Determining Step[7)*)] at $\eta = 0.07$ volt[**)], 19°C

Electrochemical Mechanism

Critical Complexes	Constants				
	I^* g cm²	$\tilde{\nu}_1^*$ cm⁻¹	$\tilde{\nu}_2^*$	$\tilde{\nu}_3^*$	$\tilde{\nu}_4^*$
$*(P_2)$	5.72×10^{-41}	124	3448	1427	126
$*(PD)$	8.58×10^{-41}	107	2994	1126	103
$*(D_2)$	11.44×10^{-41}	88	2438	1009	89

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*) Table shows $\tilde{\nu}_1^*$ *etc.* for $*(P_2)$ *etc.*, which are wave numbers respectively corresponding to $\nu^*(P_2)$ *etc.* Ref. 7 gives the constants of $*(P_2)$ and $*(PD)$ only but not those of $*(D_2)$. The I^* of $*(D_2)$ was calculated by multiplying that of $*(P_2)$ by the mass ratio 2 of $*(D_2)$ and $*(P_2)$ and $\tilde{\nu}_j^*$ of $*(D_2)$ were derived from those of $*(P_2)$ by dividing the latters by the square root $\sqrt{2}$ of the mass ratio as shown in Table 2.

**) *cf.* footnote *) on p. 78.

$*(\mathrm{P}_2)$ *etc.* around the axis through the centres of a metal atom and a water molecule situated against the metal atom⁷⁾, between which the critical complex is situated perpendicular to and symmetrically around the latter axis; $\nu_j^*(\mathrm{P}_2)$ *etc.* are j-th normal vibrational frequencies of $*(\mathrm{P}_2)$ *etc.* Factor 2 in the denominator of (32. P_2) and (32. D_2) is the symmetry number of $*(\mathrm{P}_2)$ and $*(\mathrm{D}_2)$ respectively. These constants were previously worked out⁷⁾ as shown in Table 2.

The $q_0^{*(\mathrm{P}_2)}$ *etc.* for the catalytic mechanism are expressed as⁸⁾

$$q_0^{*(\mathrm{P}_2)} = \prod_{j=1}^{5}\left[1-\exp\left\{-h\nu_j^*(\mathrm{P}_2)/kT\right\}\right]^{-1}\cdot\exp\left\{-\sum_{j=1}^{5}h\nu_j^*(\mathrm{P}_2)/2kT\right\}, \qquad (33.\ \mathrm{P}_2)$$

$$q_0^{*(\mathrm{PD})} = 2\prod_{j=1}^{5}[1-\exp\{-h\nu_j^*(\mathrm{PD})/kT]\}^{-1}\cdot\exp\{-\sum_{j=1}^{5}h\nu_j^*(\mathrm{PD})/2kT\}, \qquad (33.\mathrm{PD})$$

and

$$q_0^{*(\mathrm{D}_2)} = \prod_{j=1}^{5}\left[1-\exp\left\{-h\nu_j^*(\mathrm{D}_2)/kT\right\}\right]^{-1}\cdot\exp\left\{-\sum_{j=1}^{5}h\nu_j^*(\mathrm{D}_2)/2kT\right\}, \qquad (33.\ \mathrm{D}_2)$$

where $\nu_j^*(\mathrm{H}_2)$ *etc.* are the normal vibrational frequencies worked out⁸⁾ as shown in Table 3. The factor 2 of (33.PD) cares for the two alternative positions of $*(\mathrm{PD})$ occupying σ^*, which consists of two adjacent sites of H(a)-adsorption⁸⁾.

TABLE 3. Normal Vibrational Frequencies of Critical Complex of the Rate-determining Step*⁾ Catalytic Mechanism

Critical Complexes	Normal Vibrational Frequencies				
	$\tilde{\nu}_1^*$ cm^{-1}	$\tilde{\nu}_2^*$	$\tilde{\nu}_3^*$	$\tilde{\nu}_4^*$	$\tilde{\nu}_5^*$
$*(\mathrm{P}_2)$	936	687	1704	368	626
$*(\mathrm{PD})$	955	510	1377	323	474
$*(\mathrm{D}_2)$	662	486	1205	260	443

*⁾ Table shows $\tilde{\nu}_1^*$ *etc.* for $*(\mathrm{P}_2)$ *etc.*, which are wave numbers corresponding to $\nu_1^*(\mathrm{P}_2)$ *etc.* respectively.

The ratios $p^{*(\mathrm{PD})}/p^{*(\mathrm{P}_2)}$ and $p^{*(\mathrm{D}_2)}/p^{*(\mathrm{PD})}$ are now calculated by (31), (32) and Table 2 for the electrochemical mechanism as

$$p^{*(\mathrm{PD})}/p^{*(\mathrm{P}_2)} = 23.212, \quad p^{*(\mathrm{D}_2)}/p^{*(\mathrm{PD})} = 4.412, \quad 15°\mathrm{C} \qquad (34.\ \mathrm{E})$$

and by (31), (33) and Table 3 for the catalytic mechanism as

$$p^{*(\mathrm{PD})}/p^{*(\mathrm{P}_2)} = 12.794, \quad p^{*(\mathrm{D}_2)}/p^{*(\mathrm{PD})} = 2.886, \quad 15°\mathrm{C}. \qquad (34.\ \mathrm{C})$$

§ 5. Evaluation of $p^{\mathrm{P}^+}/p^{\mathrm{D}^+}$, $p^{\mathrm{P}_2}/p^{\mathrm{PD}}$ and $p^{\mathrm{PD}}/p^{\mathrm{D}_2}$

The factor $p^{\mathrm{P}^+}/p^{\mathrm{D}^+}$ in (29.b) and (29.c) are expressed according to (20) and

(18), as

$$\frac{p^{P^+}}{p^{D^+}}=\frac{Q^{P_2}N_{eq}^{PD}}{Q^{PD}N_{eq}^{P_2}}\,. \tag{35}$$

The value of $N_{eq}^{PD}/N_{eq}^{P_2}$ is shown on the top of Table 1. The partition functions Q^{P_2}, Q^{PD} and Q^{D_2} are given with good approximation, as

$$Q^{P_2}=\frac{(2\pi m^{P_2}kT)^{3/2}}{h^3}\cdot\frac{8\pi^2 I^{P_2}kT}{2h^2}\cdot\exp\left(-\frac{\varepsilon_0+\varepsilon_0^0(P_2)}{kT}\right), \tag{36. H$_2$}$$

$$Q^{PD}=\frac{(2\pi m^{PD}kT)^{3/2}}{h^3}\cdot\frac{8\pi^2 I^{PD}kT}{h^2}\cdot\exp\left(-\frac{\varepsilon_0+\varepsilon_0^0(PD)}{kT}\right), \tag{36. HD}$$

$$Q^{D_2}=\frac{(2\pi m^{D_2}kT)^{3/2}}{h^3}\cdot\frac{8\pi^2 I^{D_2}kT}{2h^2}\cdot\exp\left(-\frac{\varepsilon_0+\varepsilon_0^0(D_2)}{kT}\right), \tag{36. D$_2$}$$

where m^{P_2} *etc.* are masses of the molecules P_2 *etc.*, I^{P_2} *etc.* the moments of inertia of the respective molecules, ε_0 is the minimum potential energy taken common to P_2, PD and D_2[6] and $\varepsilon_0^0(P_2)$ *etc.* are zero point energies of P_2 *etc.* respectively. The factor 2 in the denominator of the second factor of Q^{P_2} or Q^{D_2} is the symmetry number. The moments of inertia are taken to be proportional to the reduced mass, *i.e.*

$$I^{P_2}:I^{PD}:I^{D_2}=1/2:2/3:1\,. \tag{37}$$

The zero point energies are derived from observations[9] as

$$\varepsilon_0^0(P_2)/hc=2168.1\text{ cm}^{-1},\quad \varepsilon_0^0(PD)/hc=1884.8\text{ cm}^{-1},$$
$$\varepsilon_0^0(D_2)/hc=1543.2\text{ cm}^{-1}\,. \tag{38}$$

where c is the light velocity.

We have from (35), (36), (37), (38) and the value of $N_{eq}^{PD}/N_{eq}^{P_2}$ on the top of Table 1

$$\frac{p^{P^+}}{p^{D^+}}=\frac{1}{2}\left(\frac{m^{P_2}}{m^{PD}}\right)^{3/2}\frac{I^{P_2}}{I^{PD}}\exp\left\{\frac{\varepsilon_0^0(PD)-\varepsilon_0^0(P_2)}{kT}\right\}\frac{N_{eq}^{PD}}{N_{eq}^{P_2}} \tag{39}$$
$$=0.00221\,,\qquad 15^\circ\text{C}.$$

The ratio p^{P_2}/p^{PD} and p^{PD}/p^{D_2} comprized in (29.b) and (29.c) are given according to (16) and the similar equation for D_2, as

$$p^{P_2}/p^{PD}=(Q^{P_2}/Q^{PD})\cdot N^{PD}/N^{P_2},\qquad p^{PD}/p^{D_2}=(Q^{PD}/Q^{D_2})\cdot N^{D_2}/N^{PD}$$

or by (36) as

$$\frac{p^{P_2}}{p^{PD}}=\frac{1}{2}\left(\frac{m^{P_2}}{m^{PD}}\right)^{3/2}\frac{I^{P_2}}{I^{PD}}\exp\left\{\frac{\varepsilon_0^0(PD)-\varepsilon_0^0(P_2)}{kT}\right\}\frac{N^{PD}}{N^{P_2}} \tag{40. a}$$

and

TABLE 4. Coefficient $f=f_S f_1 f_2$ at 15°C of the Equation $S_l/S_g=fS$

Overvoltage η*) volt	$\frac{p^{P_2}}{p^{PD}}$	$\frac{p^{PD}}{p^{D_2}}$	f_1		f_2		$f_S f_2$		$f=f_S f_1 f_2$	
			Electrochemical	Catalytic	Electrochemical	Catalytic	Electrochemical	Catalytic	Electrochemical	Catalytic
0.02	0.0024	0.0017	0.9979	0.9988	0.9956	0.9971	1.0037	1.0052	1.0016	1.0040
0.03	0.0023	0.0017	0.9990	0.9994	0.9956	0.9971	1.0032	1.0047	1.0022	1.0041
0.10	0.0019	0.0013	1.0035	1.0020	0.9921	0.9948	0.9997	1.0025	1.0032	1.0045
0.20	0.0014	0.0009	1.0092	1.0051	0.9887	0.9925	0.9969	1.0007	1.0061	1.0058
0.27	0.0014	0.0008	1.0092	1.0051	0.9878	0.9920	0.9977	1.0019	1.0069	1.0070
0.39	0.0014	0.0011	1.0092	1.0051	0.9904	0.9937	0.9965	0.9999	1.0057	1.0050
0.55	0.0015	0.0013	1.0081	1.0045	0.9921	0.9948	0.9967	0.9994	1.0047	1.0039

*) *cf.* footnote *) on p. 78.

$$\frac{p^{\mathrm{PD}}}{p^{\mathrm{D}_2}} = 2\left(\frac{m^{\mathrm{PD}}}{m^{\mathrm{D}_2}}\right)^{3/2} \frac{I^{\mathrm{PD}}}{I^{\mathrm{D}_2}} \exp\left\{\frac{\varepsilon_0^0 h\nu(\mathrm{D}_2)-\varepsilon_0^0(\mathrm{PD})}{kT}\right\} \frac{N^{\mathrm{D}_2}}{N^{\mathrm{PD}}}\,. \qquad (40.\mathrm{b})$$

§ 6. Results and Conclusion

Table 4 shows the results of calculation with special reference to the experimental condition of the foregoing work[4]. The second and third columns give the ratios $p^{\mathrm{P}_2}/p^{\mathrm{PD}}$ and $p^{\mathrm{PD}}/p^{\mathrm{D}_2}$ at each overvoltage calculated by (40) on the base of the data in Table 1, (37) and (38). The next two columns under f_1 and the subsequent two ones under f_2 show the value of f_1 and f_2 calculated by (29.b) and (29.c) from data of (34) and (39), and those of $p^{\mathrm{P}_2}/p^{\mathrm{PD}}$ and $p^{\mathrm{PD}}/p^{\mathrm{D}_2}$ in the second and the third columns both for the electrochemical and the catalytic mechanisms. The last four columns give $f_S f_2$ and $f=f_S f_1 f_2$ for the respective mechanisms as derived from the relevant data of f_1 and f_2 in the foregoing columns and those of f_S in Table 1.

We see from Table 1 and 4 that f_S or f is appreciably close to unity, so that (1) holds practically in the experimental condition of the foregoing work[4] according to (21.a) for the slow discharge mechanism or to (30.a) for the electrochemical and the catalytic mechanism.

It is noted that, if the composition of hydrogen gas is that in exchange equilibrium with the solution, f_S reduces exactly to unity as seen from (23), since both $N^{\mathrm{PD}}/N^{\mathrm{P}_2}$ and $N^{\mathrm{D}_2}/N^{\mathrm{PD}}$ equal then the respective equilibrium values and $f_1 f_2$ is unity as well according to (29.b) and (29.c), since then $p^{\mathrm{P}_2}/p^{\mathrm{PD}}=p_{eq}^{\mathrm{P}_2}/p_{eq}^{\mathrm{PD}}$, $p^{\mathrm{PD}}/p^{\mathrm{D}_2}=p_{eq}^{\mathrm{PD}}/p_{eq}^{\mathrm{D}_2}$, and $p_{eq}^{\mathrm{P}_2}/p_{eq}^{\mathrm{PD}}=p_{eq}^{\mathrm{PD}}/p_{eq}^{\mathrm{D}_2}=p^{\mathrm{P}^+}/p^{\mathrm{D}^+}$ by (20) and the similar equilibrium relation $p^{\mathrm{P}^+}p_{eq}^{\mathrm{D}_2}=p^{\mathrm{D}^+}p_{eq}^{\mathrm{PD}}$. The theorem (1) holds now exactly by (21.a) and (30) not with standing finite deuterium content and irreversible electrolysis.

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