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ISOTOPIC SEPARATION FACTOR OF SLOW DISCHARGE MECHANISM OF HYDROGEN ELECTRODE REACTION

By

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Introduction

The isotopic separation factor of hydrogen electrode reaction, as defined by the ratio of the fractional decrease of protium from the solution by electrolysis to that of deuterium, is an important criterion for the mechanism of the hydrogen electrode reaction, inasmuch as it brings about a straightforward information from the critical complex of the rate-determining step[1)2)]. It is of interest that the separation factors obtained with different metals fall into two groups, i.e. those of the factor 6~7 (nickel, silver, platinum, *etc.*) and of 3 (mercury, tin, *etc.*), which happen respectively to have lower and higher overvoltages[2)3)]. On the ground of this and other experimental results HORIUTI *et al.*[4)5)] proposed the alternative mechanisms, i.e. the catalytic mechanism (the slow recombination of adsorbed hydrogen atoms) and the electrochemical mechanism (the slow neutralization of adsorbed hydrogen molecule-ion) for the respective groups of the separation factors 6~7 and 3.

It is important that the separation factor is deduced theoretically from the respective mechanisms in agreement with experimental results[4)~8)], besides that TAFEL's relation, observed rate of hydrogen electrode reaction inclusive of its temperature coefficient are accounted for from the same basis[5)9)]. Nevertheless the above alternative mechanisms appear not at all fully accepted, but the slow discharge mechanism strongly supported against them mainly on the ground of plausible values of the TAFEL constant and the activation energy

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deduced in accordance with the latter mechanism from the energy scheme of the appropriate rate-determining step, i.e. the energy of proton or hydrogen atom involved as a function of distance from water and metal atom. Such calculation has been made by HORIUTI and POLANYI[10] and similarly by BUTLER[11], by PARSONS and BOCKRIS[12], and RÜETSCHI and DELAHAY[13] with some alternation of the basic potential functions. The separation factor of the slow discharge mechanism has not yet been deduced to provide the criterion of its validity, although practicable from the energy scheme underlying the above calculation.

This has been done in the present work as below on the very basis of such energy schemes recently proposed.

§ 1. Formulation of Separation Factor.

The separation factor of the slow discharge mechanism is expressed statistical mechanically as*)[4)-8)],

$$S=(q^{*(\mathrm{H})}/q^{*(\mathrm{D})})\,(Q^{\mathrm{HDO}}/2Q^{\mathrm{H_2O}})K\,, \tag{1}$$

where $q^{*(\mathrm{H})}$ or $q^{*(\mathrm{D})}$ is the partition function of the critical complex or the BOLTZMANN factor of the reversible work required to set up the critical complex $*(\mathrm{H})$ or $*(\mathrm{D})$ of the proton or deuteron discharge in a definite, preliminarily evacuated site, $Q^{\mathrm{H_2O}}$ or Q^{HDO} the partition function of single H_2O or HDO molecule in unit volume of gas, and K the equilibrium constant of the exchange reaction

$$\mathrm{HDO}(g)+\mathrm{H_2O}(l)=\mathrm{H_2O}(g)+\mathrm{HDO}(l)\,, \tag{2}$$

i.e.

$$K=N^{\mathrm{HDO}(l)}N^{\mathrm{H_2O}(g)}/N^{\mathrm{HDO}(g)}N^{\mathrm{H_2O}(l)}\,, \tag{3}$$

where $N^{\mathrm{H_2O}(g)}$, *etc.* and $N^{\mathrm{H_2O}(l)}$, *etc.* are concentrations in gas or in solution respectively.

The quotient $Q^{\mathrm{HDO}}/2Q^{\mathrm{H_2O}}$ is calculated as usual by the expression

$$\frac{Q^{\mathrm{HDO}}}{2Q^{\mathrm{H_2O}}}=\left\{\frac{m^{\mathrm{HDO}}}{m^{\mathrm{H_2O}}}\right\}^{\frac{3}{2}}\left\{\frac{(I_AI_BI_C)_{\mathrm{HDO}}}{(I_AI_BI_C)_{\mathrm{H_2O}}}\right\}^{\frac{1}{2}} \times\frac{\Pi_i[\exp(-h\nu_i/2kT)/\{1-\exp(-h\nu_i/kT)\}]_{\mathrm{HDO}}}{\Pi_i[\exp(-h\nu_i/2kT)/\{1-\exp(-h\nu_i/kT)\}]_{\mathrm{H_2O}}} \tag{4}$$

with the molecular constants[14] given in Table 1.

*) See Appendix 1.

TABLE 1. Molecular Constants of Water.

Molecule		H_2O	HDO
Molecular weight	m	18.015	19.024
Moments of inertia 10^{-40} g cm	I_A	1.0038	1.1969
	I_B	1.9286	3.0743
	I_C	3.0131	4.3605
Ground frequencies cm^{-1}	ν_1	3656.65	2726.73
	ν_2	3755.79	3707.47
	ν_3	1594.59	1402.20

The constant K has been observed UREY and TEAL[15], HORIUTI and OKAMOTO[16], and over a wide range of temperature by IKUSIMA and AZAKAMI[17] with the results given in Table 2.

TABLE 2. Equilibrium Constant K of the Reaction $HDO(g)+H_2O(l) = H_2O(g)+HDO(l)$.

Temperature °C	0	18	50	100	160
K	1.109	1.076	1.048	1.023	1.002

We have thus

$$S = (q^{*(H)}/q^{*(D)})\, 1.80 \exp(1.67\,\mathrm{Kcal}/RT)\, K \qquad (5)$$

or

$$S = (q^{*(H)}/q^{*(D)})\, 34 \qquad (6)$$

at room temperature.

§ 2. Factor $q^{*(H)}/q^{*(D)}$.

We will develope below the factor $q^{*(H)}/q^{*(D)}$ in (6), which involves the particulars of the critical complex of the rate-determining step of the slow discharge mechanism, i.e. the transition of a hydrogen nucleous from the initial state, i.e. that of the hydrogen nucleous H^+ attached to a water molecule, to the final state, i.e. that combined as a hydrogen atom $H(a)$ with a metal atom of the electrode.

The critical complex consisting of a hydrogen nucleus has three degrees of freedom of motion and is situated around the appropriate

saddle point of the relevant energy surface. The latter energy surface is formed from the lower of $V(H^+)$ and $V(H)$ welded together by quantum-mechanical resonance, where $V(H^+)$ or $V(H)$ is the potential energy surface of the initial or the final state. Both $V(H^+)$ and $V(H)$ to be used in the present calculation have respectively, however, a rotational symmetry around the combining line of centres of the water molecule and the metal atom involved. On this ground $V(H^+)$ or $V(H)$ is given, at the fixed distance D between centres of the water molecule and the metal atom, as a function of y and x, where y is distance along the symmetry axis from the centre of the water molecule toward that of the metal atom and x the distance from the symmetry axis. In what follows y_L will denote the value of y, which satisfies the condition, $V(H^+)=V(H)$ at $x=0$.

The condition for the saddle point situated on the intersection of $V(H^+)$ and $V(H)$ as well as just on the symmetry axis, as implied in the description of the mechanism, is stated, neglecting the resonance energy, as that

(i) $\{\partial V(H^+)/\partial y\}_{x=0,y=y_L}$ and $\{\partial V(H)/\partial y\}_{x=0,y=y_L}$ are of different sign, i.e. the potential energy surface is maximum in y-direction and that

(ii) $\kappa^* \equiv \{\partial^2 V_L/\partial x^2\}_{x=0,y=y_L} > 0$, i.e. the potential energy V_L on the intersection of the two energy surfaces, $V(H^+)$ and $V(H)$, is minimum along x at $x=0$. It has turned out that the potential function used affords a unique saddle point satisfying the above condition (i) and (ii).

The force constant κ^* is given analytically as*)

$$\kappa^* = \frac{\kappa(H^+)\partial V(H)/\partial y - \kappa(H)\partial V(H^+)/\partial y}{\partial V(H)/\partial y - \partial V(H^+)/\partial y}, \qquad (7.*)$$

where

$$\kappa(H^+) = \partial^2 V(H^+)/\partial x^2, \quad \kappa(H) = \partial^2 V(H)/\partial x^2, \qquad (7.H^+), (7.H)$$

all partial differential coefficients being referred to the configuration, $x=0$ and $y=y_L$.

Because of the axial symmetry the motion of the critical complex along x is the two-fold degenerated vibrations. The frequency ν_H of the vibration of the critical complex of protium is given as

$$\nu_H = \frac{1}{2\pi}\sqrt{\kappa^*/m_H}, \qquad (8)$$

*) See Appendix 2.

where m_H is its mass; $q^{*(H)}$ is now

$$q^{*(H)} = \left\{2\sinh(h\nu_H/2kT)\right\}^{-2}, \tag{9}$$

aside from the unimportant BOLTZMANN factor of the potential energy of the critical complex at the saddle point, which is canceled out in the factor $q^{*(H)}/q^{*(D)}$ with that of $q^{*(D)}$ according to the postulate of UREY[18)19)]. The corresponding frequency ν_D of the critical complex of deuteron and $q^{*(D)}$ are given similarly as

$$\nu_D = \frac{1}{2\pi}\sqrt{\varkappa^*/m_D} = \nu_H/\sqrt{2}, \quad q^{*(D)} = \left\{2\sinh(h\nu_D/2kT)\right\}^{-2}, \tag{10),(11}$$

and henceforth the factor $q^{*(H)}/q^{*(D)}$ in question as

$$q^{*(H)}/q^{*(D)} = \left\{\frac{\sinh(h\nu_H/2\sqrt{2}\,kT)}{\sinh(h\nu_H/2kT)}\right\}^2. \tag{12}$$

§ 3. Evaluation of the Separation Factor.

In accordance with the foregoing sections the separation factor is calculated on the basis of potential functions used by PARSONS and BOCKRIS[12)] and RÜETSCHI and DELAHAY[13)]. Both the groups of authors give $V(H^+)$ and $V(H)$ in the form

$$V(H^+) = A(r), \tag{13.H$^+$}$$

$$V(H) = A'(r') + R(r), \tag{13.H}$$

where

$$r = \sqrt{y^2+x^2}, \quad r' = \sqrt{(D-y)^2+x^2}. \tag{13.D}$$

$A(r)$ or $A'(r')$ is the attractive, MORSE function between the water molecule and the proton or between the hydrogen atom and the metal atom, i.e.

$$A(r) = A_0\left\{2\exp\left[-a(r-r_e)\right] - \exp\left[-2a(r-r_e)\right]\right\}, \tag{14}$$

$$A'(r') = A'_0\left\{2\exp\left[-a'(r'-r'_e)\right] - \exp\left[-2a'(r'-r'_e)\right]\right\}. \tag{15}$$

$R(r)$ is the repulsive potential between the hydrogen atom and the water molecule expressed by PARSONS and BOCKRIS[12)] as

$$R(r) = \left\{0.567\exp(-24.9r^2) + 0.215r\exp(-2.4r^2)\right\}10^{-10}\ \text{erg/molecule}. \tag{16}$$

TABLE 3. Separation Factor, Force Constants and MORSE Constants.

Potential functions / MORSE constants / Metals	$A(r)$ of H^+				$A'(r')$ of $H(a)$				Force constants Kcal $Å^{-2}$ mol^{-1}			Separation factor S	Basic potential function from
	$-A_0$ Kcal mol^{-1}	a $Å^{-1}$	r_e Å	y_L Å	$-A_0'$ Kcal mol^{-1}	a' $Å^{-1}$	r_e' Å	$D-y_L$ *) Å	$\kappa(H^+)$	$\kappa(H)$	κ^*		
Hg	263 **)	1.16	1.05	1.29	50.0	1.24	1.74	2.03	87.1	−18.0	21	13	PARSONS & BOCKRIS[12]
	263	1.16	1.05	1.30	52.9	1.24	1.74	2.19	88.4	−14.7	24	13	RÜETSCHI & DELAHAY[13]
Ni	263	1.16	1.05	1.28	60.2	1.64	1.48	1.68	85.5	− 8.9	31	12	" "
Ag	263	1.16	1.05	1.30	57.5	1.51	1.62	1.92	88.4	− 8.4	31	12	" "

*) The distance D between the centres of water molecule and the metal atom was taken as the sum of r_e, r_e' and the distance between the equilibrium positions of proton and hydrogen atom read from the Figure given in the respective literature.

**) This value, not being given explicity in the paper of PARSONS and BOCKRIS (Ref. 12), was determined from the energy of proton at the equilibrium position read from Fig. 1 in the latter paper and the procedure of its calculation stated there.

Constants of MORSE functions adopted by PARSONS and BOCKRIS[12] for mercury electrode, $\kappa(H^+)$, $\kappa(H)$ and κ^* worked out according to (13), (14), (15), (16) and (7), and S calculated by (8), (12) and (6) are shown in Table 3.

Fig. 1 shows the potential surfaces constructed on the same basis. The intersection L shown there by a bold line has a unique minimum on the symmetry axis, which illustrates the unique saddle point in accordance with (i) and (ii). The potential E^* along L is read graphically as

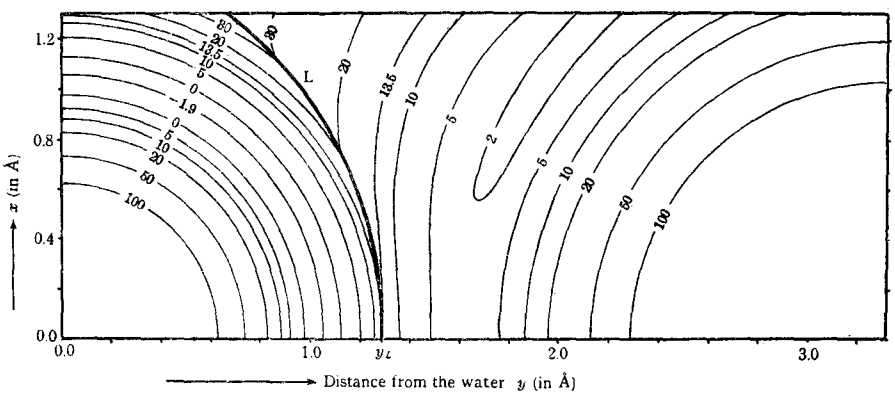


Fig. 1. Potential Surface for Mercury Electrode

$$E^* = E_0^* + \frac{1}{2}(23\ \text{Kcal}/\text{Å}^2)\,x^2,\ x \text{ in Å},$$

where E_0^* is the potential at the saddle point. The above equation gives $\kappa^* = 23$ Kcal/Å^2, in accordance, as it should be, with the analytical result in Table 3 within acceptable errors.

Table 3 shows further the similar results for Hg-, Ni- and Ag-electrodes derived from basic potential functions used by RÜETSCHI and DELAHAY[13], i.e. $R(r)$ of (16) and MORSE functions $A(r)$ and $A'(r')$ of constants given in the Table.

Table 3 shows that S derived from the slow discharge mechanism lies at 12—13 irrespective of the choice of basic potential functions of mercury or even of the kind of electrode metals.

§ 4. Concluding Remarks.

It is readily shown that the factor $q^{*(H)}/q^{*(D)}$ increases according to (12) and hence S does according to (6) with decreasing ν_H, the greatest possible value of $q^{*(H)}/q^{*(D)}$ and of S being 1/2 and 17 at $\nu_H = 0$, where

the appropriate motion is purely classical. This large limiting value of S is remarkably approached almost to the same extent by the theoretical values deduced above from the slow discharge mechanism for different electrode metals, while the theoretical value derived respectively from the catalytic or the electrochemical mechanism amounts similarly unanimously for different electrode metals only to 6—7 or 3, in accordance with experiments[4)5)6)].

The slow discharge mechanism requires on the other hand that ν_H must be 1650 or 1150 cm^{-1} to give the observed values of separation factor 3 or 6—7 in acccordance with (12) and (6). These values of ν_H correspond, according to (8), to the multiplication of the force constant $\varkappa^*$ by a factor 10 or 4, which could hardly be covered by any reasonable variation of potential functions.

This situation is to be attributed to the fact that the hydrogen nucleus of the "atomic" critical complex of the slow discharge mechanism is much more free to move compared with "molecularly" bound ones of the catalytic or the electrochemical mechanism, which should give rise, in the former case, to the too small vibrational frequencies or such zero-point energy difference at the critical state, hence to the less relative passage of deuteron through the latter and in consequence to the too large separation factor. This being thus intrinsic to the slow discharge mechanism, it could hardly be taken as realizable in hydrogen electrode reaction.

The present authors wish to express their sincere thanks to Professor J. HORIUTI for his kind suggestion of the present line of attack.

APPENDIX 1.

The speration factor S is by definition

$$S = (v_H/v_D)(N^{HDO(l)}/2N^{H_2O(l)}) ,$$

where v_H or v_D is the rate of electrolysis of protium or deuterium, which is expressed according to the general statistical mechanical theory of reaction rate[20], with special reference to the slow discharge mechanism, as

$$v_H = (kT/h)G^*\Theta_0^* q^{*(H)}/p^H , \quad v_D = (kT/h)G^*\Theta_0^* q^{*(D)}/p^D ,$$

where G^* is the number of sites for the critical complex, Θ_0^* the probability that the site is unocupied, and p^H or p^D the BOLTZMANN factor of the chemical potential of the initial complex H or D of the

discharge step which consists of a metal electron and a proton or deuteron in the solution.

Denoting the similar BOLTZMANN factor of HDO or H_2O in gas respectively by $p^{HDO(g)}$ and $p^{H_2O(g)}$, we have[20] for the interchange equilibrium, $H+HDO(g)=D+H_2O(g)$,

$$p^{H}p^{HDO(g)} = p^{D}p^{H_2O(g)}$$

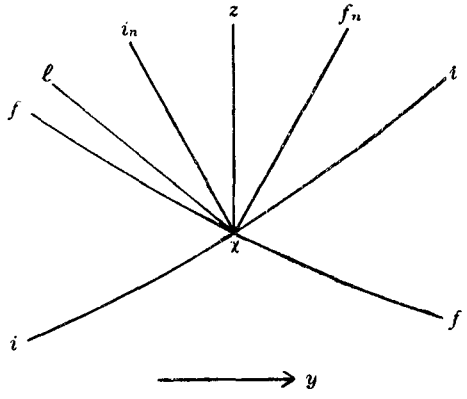
and hence

$$v_H/v_D = (q^{*(H)}/q^{*(D)})(p^{HDO(g)}/p^{H_2O(g)})$$

or (1) in the text, expressing $p^{HDO(g)}$ or $p^{H_2O(g)}$ as $p^{HDO(g)}=Q^{HDO}/N^{HDO(g)}$ or $p^{H_2O(g)}=Q^{H_2O}/N^{H_2O(g)}$.

APPENDIX 2.

Let i or f in the Figure be the potential energy $V(H^+)$ or $V(H)$ on the symmetry axis plotted against y, i_n or f_n the respective normal to i or f at the intersection χ and z the vertical through χ. The plane P of the Figure is the $x=0$ plane in the z (potential energy), x, y-space. P is now the symmetry plane to the potential surface $V(H^+)$ and $V(H)$ in the latter space because of the original axial symmetry.



The $\varkappa^*$ of (7*) is now given, in terms of geometry of the space, as the curvature of the projection of the intersection L of $V(H^+)$ and $V(H)$ on the vertical plane Z perpendicular to P through χ and $\varkappa(H^+)$ or $\varkappa(H)$ as the curvature of the intersection of $V(H^+)$ or $V(H)$ with Z at χ. Let l be the intersection of P with the plane L_l, which osculates with L at χ. L_l is perpendicular to P because of the symmetry.

According to the theorem of MEUSNIER*), we have now

$$\varkappa(H^+)\cos(i_n, z) = \varkappa_l \cos(l, i_n), \quad \varkappa(H)\cos(z, f_n) = \varkappa_l \cos(l, f_n)$$

*) Cf. e.g. BLASCHKE, *Vorlesungen über Differentialgeometrie* I, Berlin (1924), p. 57.

and

$$\kappa^* = \kappa_l \cos(l, z) ,$$

where κ_l is the curvature of L at χ and (i_n, z), *etc.* are angle measured from i_n to z, *etc.* respectively.

Noting the relation

$$(l, i_n) + (i_n, z) = (l, z)$$
$$(l, i_n) + (i_n, z) + (z, f_n) = (l, f_n)$$

by definition, we have by eliminating κ_l, (l, i_n), (l, z) and (l, f_n) from the above five equations

$$\kappa^* = \frac{\kappa(\mathrm{H}^+)\cot(i_n, z) + \kappa(\mathrm{H})\cot(z, f_n)}{\cot(i_n, z) + \cot(z, f_n)} .$$

Noting that (i_n, z) or (z, f_n) equals the angle of the inclination i or the negative inclination of f, we have (7*) in the text by translating $\cot(i_n, z)$ or $\cot(z, f_n)$ back into physical terms, i.e. into $1/\{\partial V(\mathrm{H}^+)/\partial y\}_{x=0, y=y_\mathrm{L}}$ or $-1/\{\partial V(\mathrm{H})/\partial y\}_{x=0, y=y_\mathrm{L}}$.

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