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TRITIUM SEPARATION FACTOR OF SLOW DISCHARGE MECHANISM OF HYDROGEN ELECTRODE REACTION

By

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§ 1. Introduction

The electrolytic separation factor of hydrogen isotopes is one of important criteria for the mechanism of the hydrogen electrode reaction, inasmuch as it brings about a straightforward information about the critical complex of the rate-determining step¹⁾²⁾.

In their recent paper, to be referred to as I, KEN and one of the present authors³⁾ calculated theoretically the deuterium separation factor, S_D , on the basis of the slow discharge mechanism, and showed that the mechanism is quite unsatisfactory for explaining the observed values.

The purpose of the present paper is to extend the calculation to the case of the tritium separation factor, S_T , and to confirm further the conclusion of I.

§ 2. Theoretical Expression for S_T

In I, S_D was calculated by the expression,

$$S_D = (q^{*(H)}/q^{*(D)})(Q^{HDO}/2Q^{H_2O}) K_D, \quad (I.1)^{**})$$

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

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^{**}) Eq. (1) *etc.* in I are quoted here with the numbering (I.1) *etc.*



Now the similar expression for S_T is obtained from (I.1) and (I.2) by replacing the quantities relating to the deuteron critical complex $\ast(\text{D})$ and to the HDO molecule by similar quantities for the triton complex $\ast(\text{T})$ and for the HTO molecule, respectively:

$$S_T = (q^{\ast(\text{H})}/q^{\ast(\text{T})})(Q^{\text{HTO}}/2Q^{\text{H}_2\text{O}})K_T. \quad (1)$$

The factor $Q^{\text{HTO}}/2Q^{\text{H}_2\text{O}}$ in (1) is calculated by the similar expression to (I.4) with the molecular constants⁴⁾ in Table 1, and the equilibrium constant K_T is assumed to be unity, regarding the nearly unity value of K_D . Then we have

$$S_T = 154 (q^{\ast(\text{H})}/q^{\ast(\text{T})}) \quad (2)$$

at 20°C.

TABLE 1. Molecular constants of water⁴⁾.

		H ₂ O	HTO
Product of three moments of inertia	g^3cm^6	5.87×10^{-120}	29.4×10^{-120}
Vibrational frequencies	cm^{-1}	3650.0	2290.85
		1595.0	1339.73
		3755.42	3707.91

§ 3. Potential Surface for a Pt Electrode

The calculation of the factor $(q^{\ast(\text{H})}/q^{\ast(\text{T})})$ requires the knowledge of the potential surfaces for the critical complexes. For Hg, Ni and Ag electrodes, we can make use of the surfaces computed in I, on the basis of potential functions proposed by PARSONS and BOCKRIS⁵⁾, and RÜETSCHI and DELAHAY⁶⁾. Since, however, the experimental data⁷⁾ of S_T are available only for a Pt electrode, we have also computed the potential surface for a Pt electrode following the procedures of the above authors and of I.

As described in I, the potential surface is determined by the potential energy functions for the initial and final states, $V(\text{H}^+)$ and $V(\text{H})$, and the distance D between the centres of the metal atom and the water molecule. PARSONS and BOCKRIS⁵⁾ used the following expres-

sions for $V(H^+)$ and $V(H)$;

$$V(H^+) = \phi_a + \phi_i - \phi_w + A(r) - \phi_a, \quad (\text{I. 13 } H^+)$$

$$V(H) = \phi_a + A'(r') + R(r), \quad (\text{I. 13 } H)$$

where ϕ_a is the dissociation energy of one-half mole of hydrogen (51.7 Kcal), ϕ_i the ionization energy of hydrogen (313 Kcal), ϕ_w the electronic work function of the electrode metal (5.32 eV⁸⁾ for Pt), ϕ_a the adsorption energy of hydrogen ion in the double layer, the value of which is negligible, and the other notations are the same as in I.

Since the constants in the MORSE function

$$A'(r') = A'_0 \{ 2 \exp[-a'(r'-r'_e)] - \exp[-2a'(r'-r'_e)] \} \quad (\text{I. 15})$$

has not yet been spectroscopically determined for the Pt-H molecule, we have made the following choice: A'_0 was evaluated to be -62.9 Kcal by RÜETSCHI and DELAHAY⁶⁾; a' was determined by the relation between the MORSE constants,

$$a' = \sqrt{2} \pi \nu_e \sqrt{\mu/A'_0}, \quad (3)$$

where μ and ν_e are the reduced mass and the vibrational frequency, respectively, of the molecule; r'_e and ν_e were estimated at 1.65 Å and $5.37 \times 10^{13} \text{ sec}^{-1}$, respectively, by HORIUTI and NAKAMURA⁹⁾. Thus the equation (I.15) is expressed as

$$A'(r') = -62.9 \{ 2 \exp[-1.47(r'-1.65)] - \exp[-2.94(r'-1.65)] \}, \quad (4)$$

for the Pt-H system.

Finally, the metal atom-water molecule distance D was determined on the assumption,

$$D = D(\text{Ni}) + \frac{1}{2} [d(\text{Pt}) - d(\text{Ni})],$$

where $D(\text{Ni})$ is the similar distance in the case of a Ni electrode (2.96 Å according to RÜETSCHI and DELAHAY⁶⁾), and $d(\text{Pt})$ (2.77 Å) or $d(\text{Ni})$ (2.48 Å) is the Pt-Pt or Ni-Ni distance in metallic Pt or Ni.

From the potential surface thus determined, the force constant κ^* of the critical complex $\ast(H)$ on a Pt electrode was computed similarly as I. The result is tabulated in Table 2, together with those for Hg-, Ni- and Ag-electrodes computed in I.

§ 4. Result and Discussion

Using the values of force constants in Table 2, and the expressions (I.8) and (I.9) as well as the similar ones for tritium, one can easily calculate the vibrational frequencies of the critical complexes, the partition functions, $q^{*(H)}$ and $q^{*(T)}$, in (2), and hence the values of S_T from (2). The final results are tabulated also in Table 2.

TABLE 2. Separation factor of slow discharge mechanism.

Electrode metal	Pt	Hg	Ni	Ag
Force constant κ^* Kcal \AA^{-2} mol $^{-1}$	23	21 24	31	31
Separation factor S_T	37	38 36	33	33

The MORSE function for Pt-H was determined in the present paper on some assumptions, as the spectroscopic data have not been known yet. But the value of S_T will be scarcely changed, as actual calculations show, by any reasonable variations of the MORSE constants and of D , and moreover is expected to become a little larger than the calculated values in Table 2, for the equilibrium constant K_T must be larger than unity, considering the fact that K_D has the value of 1.07 at 20°C¹⁰⁾. In fact, the slow discharge mechanism requires that the vibrational frequency ν_H of $*(H)$ must be 1130 cm $^{-1}$ in order to give the observed value of $S_T=14$, even if $K_T=1$. This value of ν_H corresponds to the multiplication of the force constant κ^* by a factor of about 5, which could hardly be covered any reasonable variation of the potential function, too.

Table 3 shows, on the other hand, the theoretical values³⁾⁹⁾¹¹⁾ of S_D as well as S_T , which were calculated on the basis of the catalytic and the electrochemical mechanisms, together with the experimental ones²⁾⁷⁾¹²⁾¹³⁾. Here one may observe that the calculated values of the separation factor depend strongly on the mechanisms, but are only slightly affected by different choices of potential functions (compare the values for Pt, Ni and Ag, of the same mechanism).

Evidently, the catalytic and the electrochemical mechanisms are successful in explaining the observed values, whereas the results of the

Tritium Separation Factor of Slow Discharge Mechanism

TABLE 3. Separation factor of various mechanisms.

Electrode metals	Separation factor		Calculated					
	Observed		Slow discharge mechanism		Catalytic mechanism		Electrochemical mechanism	
	S _D	S _R	S _D	S _R	S _D	S _R	S _D	S _R
Pt	6.9	13.4 14.7	13	37	7.2	16.1	—	—
Ni	6.7	—	12	33	6.8 7.0	15.1	—	—
Ag	6.0	—	12	33	5.9	—	—	—
Hg	3.1 3.8	—	13	36 38	—	—	3.8	5.8

slow discharge mechanism are unsatisfactory. This situation, as pointed out in I, is to be attributed to the fact that the critical complex of the slow discharge mechanism is "monatomic", and on the other hand those of the other mechanisms consist of two hydrogen atoms, which are "molecularly" bound: the former is more free to move compared with the latter, giving rise to the too small vibrational frequencies and hence the too large separation factor.

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