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# ELECTROLYTIC SEPARATION FACTOR OF TRITIUM\*

By

Juro HORIUTI and Takashi NAKAMURA

## 1. Introduction

M. L. EIDINOFF<sup>15)</sup> has recently observed the electrolytic separation factor of tritium  $S_T$ . In the present paper  $S_T$  is theoretically calculated, extending our previous calculation<sup>1)2)</sup> of the separation factor of deuterium  $S_D$ , on the basis of two different mechanisms of the hydrogen electrode process, i. e. the "catalytic mechanism" and the "electrochemical mechanism", which have heretofore been evidenced<sup>3)</sup> to be prevalent respectively on electrodes of Ni, Ag, Pt, etc. and on those of Hg, Sn, etc. Since the theory of the separation factor due to the electrochemical mechanism is given in detail in a recent article by HORIUTI, KEII and HIROTA<sup>2)</sup> (hereafter referred to as HKH), that due to the catalytic mechanism is treated here with more stress.

## 2. Theoretical Expression for $S_T$

The tritium's separation factor  $S_T$  is defined by

$$S_T = (v_H/[H]) / (v_T/[T]), \quad (1)$$

i. e. the ratio of  $v_H/[H]$ , the rate of decrease by electrolysis of protium  $v_H$  relative to its total amount  $[H]$  in the solution, to that for tritium  $v_T/[T]$ . The application of the "generalized transition state method"<sup>5)6)</sup> to the hydrogen electrode process leads now, irrespective of the mechanism of the process, to the statistical mechanical expression for  $S_T$ ,

$$S_T = (q_H^*/q_T^*) (Q_{HTO}/Q_{H_2O}) K \quad (2)$$

\*) The preliminary note of this article was published in J. Chem. Phys., **18**, 395 (1950).

1) OKAMOTO, HORIUTI and HIROTA, Sci. Pap. Inst. Phys. Chem. Research, Tokyo, **29**, 223 (1936).

2) HORIUTI, KEII and HIROTA, This journal.

3) HORIUTI and OKAMOTO, Sci. Pap. Inst. Phys. Chem. Res., **28**, 231 (1936); HIROTA and HORIUTI, *ibid.*, **30**, 151 (1936).

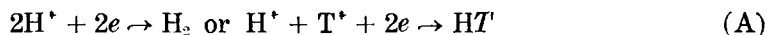
4) HORIUTI, This journal **1**, 8 (1948).

5) HORIUTI, Bull. Chem. Soc. Japan, **13**, 210 (1938); HIROTA and HORIUTI, Sci. Pap. Inst. Phys. Chem. Res., **34**, 1174 (1938).

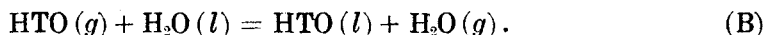
6) Ref. 4, p. 41 et seq.

*Electrolytic Separation Factor of Tritium*

where  $q_{\text{H}}^*$  or  $q_{\text{T}}^{* (1)}$  is the Boltzmann factor  $\exp(-\varepsilon/kT)$  of the reversible work  $\varepsilon$  required to bring up the critical complex<sup>(5)(6)</sup> of the rate-determining step of the electrode process,



respectively, from its reference state up to a preliminary cleared definite site on the electrode;  $Q_{\text{H}_2\text{O}}$  or  $Q_{\text{HTO}}$  is the partition function of a gaseous  $\text{H}_2\text{O}$  or  $\text{HTO}$  molecule respectively and  $K$  the equilibrium constant of the reaction,

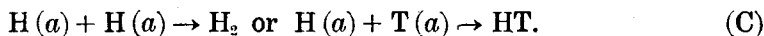


Eq. (2) is the "tritium version" of Eq. (23.8) of HKH, in which the quantities for deuterium in the latter formula are replaced by those for tritium. For further details, § 23 of HKH is referred to.

The method of calculation of the factor  $(q_{\text{H}}^*/q_{\text{T}}^*)$  in Eq. (2), which is specific to the reaction mechanism, will be described in Secs. 3 and 4 respectively for the catalytic and electrochemical mechanisms and those of the remaining factors in (2) in Sec. 5.

### 3. $(q_{\text{H}}^*/q_{\text{T}}^*)$ for the Catalytic Mechanism

The rate-determining step of this mechanism is the recombination process of the hydrogen atoms adsorbed on the electrode metal, i. e.,



The first step of computing  $q_{\text{H}}^*$  was now the determination of the potential energy for the reaction complex<sup>(6)</sup> consisting of two metal atoms  $a$  and  $b$  fixed on the electrode surface, and two H atoms 1 and 2: the application of London's approximate formula to our system at once yielded the expression for the potential energy  $V$ ,

$$\begin{aligned} V = & K_{ab} + K_{12} + K_{a1} + K_{b2} + K_{a2} + K_{b1} \\ & - \left[ \frac{1}{2}(J_{ab} + J_{12} - J_{a1} - J_{b2})^2 + \frac{1}{2}(J_{ab} + J_{12} - J_{a2} - J_{b1})^2 \right. \\ & \left. + \frac{1}{2}(J_{a1} + J_{b2} - J_{a2} - J_{b1})^2 \right]^{\frac{1}{2}}, \quad (3) \end{aligned}$$

where  $J_{ab}$  etc. and  $K_{ab}$  etc. were the exchange and the Coulomb energies between the metal atoms  $a$  and  $b$  etc. computed according to EYRING and POLANYI'S semi-empirical method. The potential energy surface thus obtained was found to have a saddle point, at which the surface

was expanded in terms of the coordinates of the H atoms  $x_i$ 's and expressed in the quadratic form,

$$V = V_0 + \sum_{i,j} A_{ij} (x_i - x_i^0) (x_j - x_j^0), \quad (i, j = 1, \dots, 6), \quad (4)$$

where  $V_0$  and  $(x_1^0, \dots, x_6^0)$  were the potential energy and the coordinates of the saddle point respectively. By introducing the normal coordinates  $q_i$ 's<sup>1)</sup> with their origin at the saddle point, the expression for  $V$  reduced into the form,

$$V = V_0 + \frac{1}{2} \sum \lambda_i q_i^2, \quad (i = 0, \dots, 5), \quad (5)$$

where all the coefficients  $\lambda_i$ 's except  $\lambda_0$  were positive. The hypersurface  $q_0 = 0$  in the partial configuration space  $(x_1, \dots, x_6)$  was taken the approximate critical surface,<sup>5)6)</sup> thus  $\nu_i = \lambda_i^{1/2}/2\pi$  ( $i = 0, \dots, 5$ ) were the normal frequencies of the critical complex, of which  $\nu_0$  was imaginary one.\*) Using  $\nu_1, \dots, \nu_5$ ,  $q_{\text{H}}^*$  was now computed as that,

$$q_{\text{H}}^* = \exp(-V_0/kT) \prod_{i=1}^5 \left[ 2 \sinh(h\nu_i/2kT) \right]^{-1}. \quad (6)$$

The  $\nu_i$ 's for the complex HT\* (or HD\*), and consequently  $q_{\text{T}}^*$  (or  $q_{\text{H}}^*$ ) were computed according to UREY's assumption<sup>7)</sup> that the potential energy is invariant with the isotopic exchange.

The above calculation was made for Ni and Pt electrodes. Table 1 and 2 show the fundamental data used in calculating  $J$ 's and  $K$ 's in Eq. (3); i. e. the constants for the MORSE functions

$$D_e (e^{-2a(r-r_e)} - 2e^{-a(r-r_e)}), \quad (7)$$

TABLE 1

Bonds	$D_e$ (Kcal)	$a$ (A <sup>-1</sup> )	$r_e$ (A)	Percentages of Coulomb energy
H—H	109.1	1.95	0.74	11 %
Ni—H	60.0	1.60	1.48	24 %
Pt—H	60.0	1.50	1.65	26 %

\*) The tunnel effect correction derived in the previous paper (Ref. 1) from this imaginary frequency  $\nu_0$  according to the WIGNER's method (Zeits. f. phys. Chem. B 19, 204 (1932)), was not applied here, since the method was invalidated in the present case of large  $\nu_0$  ( $\nu_0 \approx 1000 \text{ cm}^{-1}$ ; cf. R. P. Bell, Trans. Faraday Soc., 34, 259 (1938)).

7) UREY and RITTENBERG, J. Chem. Phys., 1, 137 (1933).

*Electrolytic Separation Factor of Tritium*

TABLE 2

Bonds	Interatomic distances	$J$ (kcal)	$K$ (kcal)
Ni—Ni	3.52 Å	13.0	7.6
Pt—Pt	3.93 Å	10.0	6.0

the percentages of the Coulomb energy, etc. The data for Ni electrode was the same as that used in Ref.1. The MORSE constants for Pt—H, not being spectroscopically known so far, were determined as follows:  $D_e$  was taken as the mean of the heat of adsorption  $X$  of  $H_2$  on Pt (18 kcal/mole)<sup>8)</sup> and the heat of dissociation  $D_e$  of  $H_2$  (102 kcal/mole), i. e. as  $D_e = \frac{1}{2}(X + D)$ ;  $r_e$  was taken the mean of that derived from atomic radii in SLATER's table<sup>9)</sup> according to his relation<sup>9)</sup> between interatomic distances and radii of atoms involved, and the other obtained from the assumption that  $r_e = r'_e + \frac{1}{2}(d_{Pt} - d_{Ni})$ , where  $r'_e$  was the Ni—H distance in Ni—H molecule (1.48 Å),<sup>1)</sup> and  $d_{Pt}$  (=2.77 Å) or  $d_{Ni}$  (=2.48 Å) Pt—Pt or Ni—Ni distance in metallic Pt or Ni; the vibrational frequency  $\omega_e$  for Pt—H molecule was determined by the empirical relation due to MORSE and MULLIKEN,<sup>10)</sup>

$$\omega_e r_e^3 (4m_1 m_2 / (m_1 + m_2))^{\frac{1}{2}} = \text{const.} = 3 \times 10^{-21} \text{ cm}^2,$$

where  $m_1$  and  $m_2$  were the masses of Pt and H atoms respectively, and  $\omega_e$  and  $r_e$  given in  $\text{cm}^{-1}$  and cm respectively; finally  $a$  was determined by the relation between the MORSE constants,<sup>11)</sup>

$$a = 1.218 \times 10^7 \omega_e (\mu / D_e)^{\frac{1}{2}},$$

where  $a$  as well as  $D_e$  was expressed in  $\text{cm}^{-1}$ , and  $\mu$  the reduced mass of the molecule (gram/mole). The percentage of Coulomb energy for Pt—H bond (Table 1) was taken as the mean of that for H—H (11%)<sup>1)</sup> and that for Pt—Pt (26%).<sup>12)</sup> The  $\nu_i$ 's thus calculated for the complexes

8) KWAN, this journal, 1, 81. (1949).

9) SLATER, Phys. Rev., 36, 57 (1930).

10) MORSE, *ibid.*, 34, 57 (1929).

11) HERZBERG, "Molecular Spectra and Molecular Structure I", (1939).

12) ROSEN and IKEHARA, Phys. Rev., 43, 5 (1935).

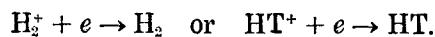
H<sub>2</sub><sup>\*</sup>, HD<sup>\*</sup> and HT<sup>\*</sup> are given in Table 3.

TABLE 3.

Electrodes	Complexes	Frequencies (cm <sup>-1</sup> )					
		ν <sub>1</sub>	ν <sub>2</sub>	ν <sub>3</sub>	ν <sub>4</sub>	ν <sub>5</sub>	ν <sub>6</sub>
Ni	H <sup>*</sup>	1704	936	687	607	398	839±
	HD <sup>*</sup>	1377	955	510	544	314	676±
	HT <sup>*</sup>	1374	803	449	530	263	614±
Pt	H <sup>*</sup>	1362	926	815	682	197	1301±
	HD <sup>*</sup>	1193	802	632	593	160	1103±
	HT <sup>*</sup>	1149	723	528	563	144	1082±

#### 4. ( $q_{\text{H}}^*/q_{\text{T}}^*$ ) for the Electrochemical Mechanism

The rate-determining step of this mechanism is the neutralization of a hydrogen molecule-ion adsorbed on the electrode-solution interface, i.e.



The previous calculation of the deuterium's separation factor  $S_{\text{D}}$  in this case,<sup>2)</sup> was simply transposed to tritium on the basis of UREY's assumption<sup>7)</sup>: Eq. (23.7) and (19.2) of HKH led to the expression for ( $q_{\text{H}}^*/q_{\text{T}}^*$ ),

$$\left(\frac{q_{\text{H}}^*}{q_{\text{T}}^*}\right) = \frac{1}{2} \left(\frac{I}{I'}\right)^{\frac{1}{2}} \frac{II \sum_{i=1}^4 2 \sinh(h\nu'_i/2kT)}{II \sum_{i=1}^4 2 \sinh(h\nu_i/2kT)}, \quad (i=1, \dots, 4), \quad (8)$$

where  $\nu_i$  and  $I$  were the frequencies and the moments of inertia of the critical complex H<sub>2</sub><sup>\*</sup>, and  $\nu'_i$  and  $I'$  those for the complex HT<sup>\*</sup>. These frequencies and the moments of inertia were calculated on the basis of the potential derived in HKH for the Hg electrode polarized against the *N* calomel electrode by -1.26 volt in *N*/10 HCl, the result being given in Table 4.

TABLE 4

Electrodes	Complexes	Frequencies (cm <sup>-1</sup> )				Moments of inertia (g. cm <sup>2</sup> )
Hg	H <sub>2</sub> <sup>*</sup>	3388	1516	163	105	6.16 × 10 <sup>-41</sup>
	HD <sup>*</sup>	2905	1231	134	91	9.24 × 10 <sup>-41</sup>
	HT <sup>*</sup>	2755	1059	115	86	12.32 × 10 <sup>-41</sup>

*Electrolytic Separation Factor of Tritium*

5.  $Q_{\text{H}_2\text{O}}$ ,  $Q_{\text{HTO}}$  and  $K$ .

The  $Q_{\text{H}_2\text{O}}$  and  $Q_{\text{HTO}}$  (or  $Q_{\text{HDO}}$ ) were calculated according to the expression :

$$Q = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 (2\pi IkT)^{\frac{3}{2}}}{sh^3} \exp\left(-\frac{\epsilon_0}{kT}\right) \quad (9)$$

where  $m$ ,  $s$ ,  $I$  and  $\epsilon_0^{(*)}$  are the mass, symmetry number, geometrical mean of the three moments of inertia, and zero-point vibrational energy of the water molecules respectively. The molecular constants used here (Table 5) were due to W. F. LIBBY.<sup>13)</sup> The equilibrium constant  $K$ , not being measured as yet, was taken unity regarding the nearly unity value of that for deuterium. (1.04 at 25°C<sup>13)</sup>)

TABLE 5

	I × 10 <sup>40</sup> (g. cm <sup>2</sup> )	ε <sub>0</sub> (cm <sup>-1</sup> )
H <sub>2</sub> O	5.87	4631
HDO	16.6	4020
HTO	29.4	3762

6. Results

The separation factors  $S_T$  (as well as  $S_D^{**})$  thus calculated are tabulated in Table 6 and compared with the experimental results given in the parentheses.

Finally the authors are grateful to Mr. KEII for his collaboration in some part of the present work.

TABLE 6.  $S_T$  and  $S_D$  at 20°C

	Catalytic mechanism		Electrochemical mechanism
	Ni electrode	Pt electrode	Hg electrode
$S_D$	6.8 (6.7) <sup>14)</sup>	7.2 (6.9) <sup>14)</sup>	3.8 (3.1) <sup>4)</sup>
$S_T$	15.1 (none)	16.1 (14.0) <sup>15)</sup>	5.8 (none)

\*) The considerably large  $\epsilon_0$  of the water molecule allows us to use the expression  $\exp(-\epsilon_0/kT)$  for the vibrational partition function at the room temperature.

\*\*\*) The slight difference between the value of  $S_D$  for Ni electrode here and that in Ref. 1 is due to the adoption of the new molecular constants for the water molecules (Ref. 13) and the omission of the tunneling effect correction (cf. p. 76, footnote).

13) DENNISON and DARLING, *Phys. Rev.*, **57**, 128 (1940); LIBBY, *J. Chem. Phys.*, **11**, 101 (1943).

14) HORIUTI and OKAMOTO, *Bull. Chem. Soc. Jap.*, **10**, 503 (1935).

15) EIDLHOFF, *J. Am. Chem. Soc.*, **69**, 2507 (1947).