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ELECTROLYTIC SEPARATION FACTOR OF TRITIUM*

By

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1. Introduction

M. L. EIDINOFF¹⁵⁾ has recently observed the electrolytic separation factor of tritium S_T . In the present paper S_T is theoretically calculated, extending our previous calculation¹⁾²⁾ 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 evidenced¹⁾³⁾ 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, KEI and HIROTA²⁾ (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"⁵⁾⁶⁾ to the hydrogen electrode process leads now, irrespective of the mechanism of the process, to the statistical mechanical expression for S_T ,

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

*) 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, KEI 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 (1933); HIROTA and HORIUTI, Sci. Pap. Inst. Phys. Chem. Res., **34**, 1174 (1938).

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

where q_H^* or $q_T^{* (1)}$ is the Boltzmann factor $\exp(-\epsilon/kT)$ of the reversible work ϵ required to bring up the critical complex⁽⁵⁾⁽⁶⁾ 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_{H_2O} or Q_{HTO} is the partition function of a gaseous H_2O or 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_H^*/q_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_H^*/q_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_H^* was now the determination of the potential energy for the reaction complex⁽⁶⁾ 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 's¹⁾ 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 λ_i 's except λ_0 were positive. The hypersurface $q_0 = 0$ in the partial configuration space $(x_1, \dots, x_6)$ was taken the approximate critical surface,^{5,6)} thus $\nu_i = \lambda_i^{1/2}/2\pi$ ($i = 0, \dots, 5$) were the normal frequencies of the critical complex, of which ν_0 was imaginary one.^{*)} Using $\nu_1, \dots, \nu_5$, q_H^* was now computed as that,

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

The ν_i 's for the complex HT^* (or HD^*), and consequently q_T^* (or q_H^*) were computed according to UREY's assumption⁷⁾ 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 ⁻¹)	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 ν_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 ν_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).

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)⁸⁾ 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 table⁹⁾ according to his relation⁹⁾ 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),¹⁾ 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 ω_e for Pt—H molecule was determined by the empirical relation due to MORSE and MULLIKEN,¹⁰⁾

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

where m_1 and m_2 were the masses of Pt and H atoms respectively, and ω_e and r_e given in cm^{-1} and cm respectively; finally a was determined by the relation between the MORSE constants,¹¹⁾

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

where a as well as D_e was expressed in cm^{-1} , and μ 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%)¹⁾ and that for Pt—Pt (26%).¹²⁾ The ν_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_2^* , HD^* and HT^* are given in Table 3.

TABLE 3.

Electrodes	Complexes	Frequencies (cm^{-1})					
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_0
Ni	H^*	1704	936	687	607	398	839 $\frac{1}{2}$
	HD^*	1377	955	510	544	314	676 $\frac{1}{2}$
	HT^*	1374	803	449	530	263	614 $\frac{1}{2}$
Pt	H^*	1362	926	815	682	197	1301 $\frac{1}{2}$
	HD^*	1193	802	632	593	160	1103 $\frac{1}{2}$
	HT^*	1149	723	528	563	144	1082 $\frac{1}{2}$

4. (q_H^*/q_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_D in this case,²⁾ was simply transposed to tritium on the basis of UREY's assumption⁷⁾: Eq. (23.7) and (19.2) of HKH led to the expression for (q_H^*/q_T^*) ,

$$(q_H^*/q_T^*) = \frac{1}{2} \left(\frac{I}{I'} \right)^{\frac{1}{2}} \frac{H 2 \sinh(h\nu'_i/2kT)}{H 2 \sinh(h\nu_i/2kT)}, \quad (i=1, \dots, 4), \quad (8)$$

where ν_i and I were the frequencies and the moments of inertia of the critical complex H_2^* , and ν'_i and I' those for the complex HT^* . 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^{-1})				Moments of inertia ($g \cdot cm^2$)
Hg	H_2^*	3388	1516	163	105	6.16×10^{-41}
	HD^*	2905	1231	134	91	9.24×10^{-41}
	HT^*	2755	1059	115	86	12.32×10^{-41}

Electrolytic Separation Factor of Tritium

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

The $Q_{\text{H}_2\text{O}}$ and Q_{HTO} (or Q_{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.¹³⁾ 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°C¹³⁾)

TABLE 5

	$I \times 10^{40}$ (g. cm ²)	ϵ_0 (cm ⁻¹)
H ₂ 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. KEN 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) ¹⁴⁾	7.2 (6.9) ¹⁴⁾	3.8 (3.1) ⁴⁾
S_T	15.1 (none)	16.1 (14.0) ¹⁵⁾	5.8 (none)

*) The considerably large ϵ_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) EHDENOFF, J. Am. Chem. Soc., 69, 2507 (1947).