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北海道大学触媒研究所紀要 HUSCAP
TRITIUM SEPARATION FACTOR OF SLOW
DISCHARGE MECHANISM OF
HYDROGEN ELECTRODE REACTION

By

Takuro KODERA and Takashi SAITO

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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 step.\(^{(1,2)}\)

In their recent paper, to be referred to as I, KEII and one of the present authors\(^{(3)}\) 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,

\[
S_D = \left( \frac{q^{*(H)}(Q_H)}{q^{*(D)}(Q_D)} \right) \left( \frac{Q_H}{2Q_D} \right) K_D, \tag{1.1}^{(*)}
\]

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, \(Q_H^0\) or \(Q_D^0\) the partition function of a single \(H_2O\) or \(HD_2O\) molecule in unit volume of gas, and \(K_D\) the equilibrium constant of the exchange reaction.

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\(^{(*)}\) T. K.: Department of Chemistry, Faculty of Science, Hokkaido University.

T. S.: Research Institute for Catalysis, Hokkaido University.

\(^{(**)}\) Eq. (1) etc. in I are quoted here with the numbering (I.1) etc.
HDO (g) + H\textsubscript{2}O (l) = H\textsubscript{2}O (g) + HDO (l). \hspace{1cm} (I.2)

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 $\star$\textsubscript{(D)} and to the HDO molecule by similar quantities for the triton complex $\star$\textsubscript{(T)} and for the HTO molecule, respectively:

$$S_T = \left(\frac{q^{\star\textsubscript{(H)}}}{q^{\star\textsubscript{(T)}}}\right)\left(\frac{Q^{\text{HTO}}}{2Q^{\text{HDO}}}\right) K_T. \hspace{1cm} (1)$$

The factor $Q^{\text{HTO}}/2Q^{\text{HDO}}$ in (1) is calculated by the similar expression to (1.4) with the molecular constants\textsuperscript{5} 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

$$S_T = 154 \left(\frac{q^{\star\textsubscript{(H)}}}{q^{\star\textsubscript{(T)}}}\right) \hspace{1cm} (2)$$

at 20°C.

<table>
<thead>
<tr>
<th>TABLE 1. Molecular constants of water\textsuperscript{5}.</th>
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<tbody>
<tr>
<td>Product of three moments of inertia g\textsuperscript{2}cm\textsuperscript{4}</td>
</tr>
<tr>
<td>5.87×10\textsuperscript{-19}</td>
</tr>
<tr>
<td>Vibrational frequencies cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>1595.0</td>
</tr>
<tr>
<td>3755.42</td>
</tr>
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§ 3. Potential Surface for a Pt Electrode

The calculation of the factor $(q^{\star\textsubscript{(H)}}/q^{\star\textsubscript{(T)}})$ 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 Bockris\textsuperscript{5}, and Rüetschi and Delahay\textsuperscript{6}. Since, however, the experimental data\textsuperscript{7} 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, $V(H^+)$ and $V(H)$, and the distance $D$ between the centres of the metal atom and the water molecule. Parsons and Bockris\textsuperscript{5} used the following expres-
sions for $V(H^+)$ and $V(H)$:

$$V(H^+) = \phi_d + \phi_e - \phi_w + A(r) - \phi_a,$$  \hspace{1cm} (I. 13 H$^+$)

$$V(H) = \phi_d + A'(r') + R(r),$$  \hspace{1cm} (I. 13 H)

where $\phi_d$ is the dissociation energy of one-half mole of hydrogen (51.7 Kcal), $\phi_e$ the ionization energy of hydrogen (313 Kcal), $\phi_w$ the electronic work function of the electrode metal (5.32 eV$^o$ for Pt), $\phi_a$ 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

$$A'(r') = A'_e \left[ 2 \exp \left( -a' (r'-r'_e) \right) - \exp \left( -2a' (r'-r'_e) \right) \right],$$  \hspace{1cm} (I. 15)

has not yet been spectroscopically determined for the Pt-H molecule, we have made the following choice: $A'_e$ was evaluated to be $-62.9$ Kcal by RÜTSCHI and DELAHAY$^o$; $a'$ was determined by the relation between the Morse constants,

$$a' = \sqrt{2 \pi \nu_e \mu/|A'_e|},$$  \hspace{1cm} (3)

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

$$A'(r') = -62.9 \left[ 2 \exp \left( -1.47 (r'-1.65) \right) - \exp \left( -2.94 (r'-1.65) \right) \right],$$  \hspace{1cm} (4)

for the Pt-H system.

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

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

where $D(Ni)$ is the similar distance in the case of a Ni electrode (2.96 Å according to RÜTSCHI and DELAHAY$^o$), and $d(Pt)$ (2.77 Å) or $d(Ni)$ (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 $k^*$ of the critical complex $\kappa(H)$ 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 (1.8) and (1.9) 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.

<table>
<thead>
<tr>
<th>Electrode metal</th>
<th>Pt</th>
<th>Hg</th>
<th>Ni</th>
<th>Ag</th>
</tr>
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<tbody>
<tr>
<td>Force constant</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K^*$ Kcal Å$^{-2}$ mol$^{-1}$</td>
<td>23</td>
<td>21</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>Separation factor</td>
<td>$S_T$</td>
<td>37</td>
<td>38</td>
<td>33</td>
</tr>
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</table>

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°C$^{[9]}$. In fact, the slow discharge mechanism requires that the vibrational frequency $\nu_H$ 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 $\nu_H$ corresponds to the multiplication of the force constant $K^*$ 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 values$^{[9,11]}$ 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 ones$^{[9,12,13]}$. 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.

<table>
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<tr>
<th>Electrode metals</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S₀</td>
<td>S₁</td>
</tr>
<tr>
<td>Pt</td>
<td>6.9</td>
<td>13.4</td>
</tr>
<tr>
<td>Ni</td>
<td>6.7</td>
<td>-</td>
</tr>
<tr>
<td>Ag</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>3.1</td>
<td>3.8</td>
</tr>
</tbody>
</table>

The separation factors calculated for the 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.

The present authors wish to express their sincere thanks to Professor J. Horiuti for his valuable advice and discussion on the present work.

References

3) KELI and KODERA, this Journal 5, 105 (1957).
8) WHITNEY, Phys. Rev. 50, 1154 (1936).