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VARIATION WITH POTENTIAL OF ELECTROLYTIC HYDROGEN-DEUTERIUM SEPARATION FACTOR ON PLATINUM IN AQUEOUS SULFURIC ACID

By

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The hydrogen-deuterium separation factor S_f in the electrolytic hydrogen evolution reaction,



is defined as

$$S_f \equiv \frac{V_f(\text{H})}{1 - X^s} \bigg/ \frac{V_f(\text{D})}{X^s}, \quad (2)$$

where $V_f(\text{H})$ and $V_f(\text{D})$ are, respectively, the forward unidirectional rates of transfer of light hydrogen and of deuterium, and X^s is the atomic fraction of deuterium in aqueous electrolyte. This quantity S_f has been widely accepted as characteristic of the mechanism of the reaction (1), and therefore many efforts have been made toward both the experimental determination^{1,2)} and the theoretical interpretation³⁻⁵⁾ of the S_f -values.

According to HORIUTI, the value of S_f should be 3 or 7 approximately, depending on whether the reaction (1) obeys the electrochemical mechanism³⁾ (slow neutralization of hydrogen molecule-ions) or the catalytic mechanism⁴⁾ (slow recombination of hydrogen adatoms), but practically independent of the kind of the electrode metal. With a platinum electrode, it has been concluded⁶⁾ that the electrochemical mechanism is operative near the reversible electrode potential, it switches over to the catalytic one as the cathodic overpotential increases, but the electrochemical mechanism is restored upon further increase in the overpotential. It follows that S_f on Pt should have a value of *ca.* 3 near the reversible potential, should increase with the cathodic overpotential up to a maximum value of *ca.* 7, and then decrease toward *ca.* 3 with further increase in overpotential. FUKUDA and HORIUTI²⁾ measured the value of S_f on Pt in aqueous sulfuric acid and observed that S_f actually changes with the overpotential (*cf.* Fig. 1), in agreement with the above theoretical prediction, in the range of moderate overpotentials. The behavior

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at higher overpotentials was unclear, due to increased experimental difficulties.

It was the aim of this work to reproduce the relation between S_f and overpotential experimentally. Especially, it was hoped to confirm the earlier result that the value of S_f near the reversible potential is smaller than the value of the partition coefficient S (4.1 at 15°C) of deuterium between gaseous hydrogen and aqueous electrolyte; $S_f < S$ indicates that deuterium is more readily ionized than light hydrogen in that potential region (see Eq. (4) below).

The experimental apparatus and procedure were essentially the same as those used previously.²⁾ Experiments were carried out with two cells; one (cell I) was identical with that described before²⁾ but the other (cell II) was specially designed for electrolysis at high current densities. The electrolytic solution was aqueous sulfuric acid, about 1N, and its deuterium content was about 10 atom per cent throughout. The potential of the test electrode was measured against a reversible hydrogen electrode in the same system using a glass electrode pH meter (Metrohm, E-300, with an input resistance *ca.* 10^{15} ohm). The potential was maintained at a desired constant value by means of a potentiostat (Nichia Keiki Co., HP-E5) in the electrolysis at low overpotentials, or by controlling manually the current density

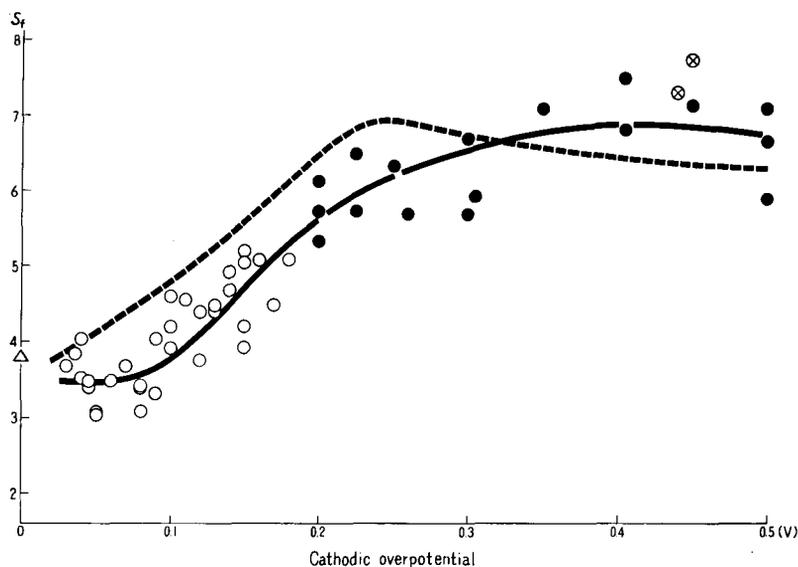


Fig. 1. Variation of Separation factor S_f with cathodic overpotential.

○ : obtained potentiostatically with cell I

● : obtained potentiostatically with cell II

⊗ : obtained galvanostatically with cell II

△ : evaluated from separation factor in reverse direction (see text)

The dotted line represents the result obtained by FUKUDA and HORIUTI.²⁾

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at high overpotentials. The deuterium content in the evolved hydrogen was determined with a mass spectrometer (Hitachi, RMD-3).

The values of S_f thus obtained are plotted against the overpotential in Fig. 1, where open (○) and closed (●) circles represent the S_f -values obtained potentiostatically with cell I and cell II, respectively, and circles with a cross mark (⊗) represent those obtained with cell II under the condition of constant current and constant overpotential, which was realized after prolonged electrolysis at constant current density. (For the value at the reversible potential Δ , see below.)

It is clearly seen from Fig. 1 that the value of S_f changes from *ca.* 3 near the reversible potential to *ca.* 7 in the high overpotential region. These results agree essentially with those of FUKUDA and HORIUTI²⁾ (represented by a dotted line), though our S_f -values are slightly lower than theirs. The scatter of the data was of the same order of magnitude as in their results.

It is thus confirmed that S_f near the reversible potential is smaller than 4.1, *i.e.*, smaller than the partition coefficient at 15°C*) of deuterium between aqueous electrolyte and gaseous hydrogen and with sufficiently low deuterium contents in both the phases.⁷⁾ Now, in the case that gaseous hydrogen is equilibrated with respect to the reaction,



and both X^g , the atomic fraction of deuterium in the gaseous hydrogen, and X^s are sufficiently low, the following relation has been shown to hold:⁸⁾

$$S_b(X^g \simeq 0) = S_f/S, \quad (4)$$

where $S_b(X^g \simeq 0)$ is the value at $X^g \simeq 0$ of the hydrogen-deuterium separation factor S_b in the electrolytic hydrogen *ionization* reaction defined as

$$S_b \equiv \frac{V_b(\text{H})}{1 - X^g} \bigg/ \frac{V_b(\text{D})}{X^g},$$

and $V_b(\text{H})$ and $V_b(\text{D})$ are, respectively, the unidirectional rates of transfer of light hydrogen and deuterium by the backward reaction of (1). Consequently, the above S_f -value near the reversible potential gives

$$S_b(X^g \simeq 0) = 0.8_5 \pm 0.1,$$

i.e., deuterium is more readily ionized than light hydrogen on Pt at low overpotentials.

It has recently been established⁹⁾ by ENYO and YOKOYAMA that S_b is validly determined from the value of the mixed potential in a system composed of

*) Interpolated from the values^{2,7)} at 5°C and 20°C assuming a linear relationship between $\log S$ and $1/T$.

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deuterium-containing hydrogen and light water, provided that the gaseous hydrogen is equilibrated with respect to the reaction (3) and that the stoichiometric number of the rate-determining step of the reaction (1) is known. On a platinum hydrogen electrode in a system composed of light water containing sulfuric acid and "pure" deuterium gas ($X^g=0.998$) which was preliminarily equilibrated at 300°C, the value of S_b has been determined⁹⁾ as 1.04 ± 0.01 at 22°C, on the basis of a value¹⁰⁾ of unity for the stoichiometric number. Further, it can be shown¹¹⁾ that S_b obtained at $X^g \simeq 1$ under this condition is connected with S_f on one and the same electrode in the same environment as

$$S_b(X^g \simeq 1) = (S_f/S) \cdot (4/K), \quad (5)$$

where K is the equilibrium constant (3.7 at 300°C)¹²⁾ of the reaction (3). Now, assuming that S_f has no correlation with X^g , and eliminating S_f from Eqs. (4) and (5), one obtains the following value for S_b :

$$S_b(X^g \simeq 0) = \frac{K}{4} S_b(X^g \simeq 1) = 0.96 \pm 0.01.$$

Incidentally, this value of S_b leads to $S_f=3.8$ (shown by \triangle in Fig. 1) when one uses a value of $S=3.9$ (at 22°C, as obtained in the above interpolation).

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