A Research on Isotopic Composition of Evolved Hydrogen Molecules with Special Reference to the Mechanism of Nickel Cathode

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Although a number of research has been published on the separation factor of hydrogen evolved at the electrolysis of aqueous solutions, no attention has been paid on the composition of isotopically different molecules, i.e., H_2 HD and D_2. However, by the following reasoning, it seems very important to investigate if the composition coincides with the one expected by the gaseous equilibrium:

$$H_2 + D_2 \leftrightarrows 2HD \qquad (1)$$

In the case of the discharge mechanism (A), evolved hydrogen must be equilibrated by the practical equilibrium of the recombination step of statistically independent hydrogen atoms formed by the rate-determining step $H^+ + e \rightarrow H$ of this mechanism. On the other hand, in the case of the catalytic (B) or the electrochemical (C) mechanism the evolved hydrogen need not be equilibrated, inasmuch

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TABLE I. SEPARATION FACTOR AND ISOTOPIC COMPOSITION EVOLVED AT THE NICKEL ELECTRODE AT 0°C

Exp. no.	Current density mA/cm^2	D atom %	Separation factor α	$K(\text{obs})=\frac{[HD]^2}{[H_2][D_2]}$
41	25.3	30.3	4.3	2.8
42	50.6	25.1	5.6	2.7
43	84.3	21.6	6.6	2.7
44	147.3	20.5	7.3	2.7
45	190	21.4	7.4	2.8

* a) All the data of the columns 3,4 and 5 are the means of two measurements except for No. 41.

b) D atom% of the original solution: 65.2%.

as the rate is governed in either case by the step of formation of the hydrogen molecule itself, which is not of course in equilibrium.

It is interesting therefore to demonstrate the above consideration experimentally on some cathode. As the first example, nickel electrode has been taken up, because the mechanism of this electrode is not yet determined in spite of the effort of many researchers. The electrolysis was carried out on 1 N sodium carbonate solution with the cathode of nickel plate (surface area, 0.48 cm^2) and the anode of platinum wire. Deuterium content in the original solution was 65.2% (atom%). The ratio H_2 : HD : D_2 of the hydrogen evolved at the cathode as well as the separation factor α, defined by $(H/D)_{\text{gas}}/(H/D)_{\text{sol}}$, were determined mass-spectrometrically.

The result obtained at 0°C is summarized in Table I. It is shown that α increases with current density and approaches to the value of 7.4 which is nearly equal to that hitherto obtained by the electrolysis of aqueous solution of low deuterium concentration in the case of nickel cathode[1]. It is noteworthy on the other hand that the factor $K(\text{obs.})=[HD]^2/[H_2][D_2]$ is 2.7 or 2.8 which is less than the K (equil.), i. e., 3.25 at 0°C[2].

Such being the situation, the discharge mechanism (A) can not be accepted so far as nickel cathode is concerned. Although the mechanism (B) or (C) is reasonable, some other experimental fact must be resorted to for the discussion between the mechanisms. From the reason that no positive proof for the mechanism (C) has been found until now, the catalytic mechanism (B)[1,3] may be accepted.

Detailed research on other electrodes is now in progress.

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