ACTION OF ATOMIC HYDROGEN ON POLARIZED ELECTRODES IN ELECTROLYTE SOLUTIONS

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In the present work we used a new method of studying hydrogen overvoltage. This method consists of the action of hydrogen atoms, obtained from some foreign source, on electrodes in a stationary state or with a current flowing. The introduction of atomic hydrogen into the reaction sphere and the study of the nature of its subsequent behavior are of great interest,as H atoms are intermediate units in the electrolytic preparation of hydrogen from its ions or water molecules, and existing theories of hydrogen overvoltage treat the role of hydrogen atoms in this process differently.

We studied the action of atomic hydrogen on electrodes on an apparatus which was a modification of that of Harteck and Roeder [1] for investigating the reactions of H atoms in liquids.

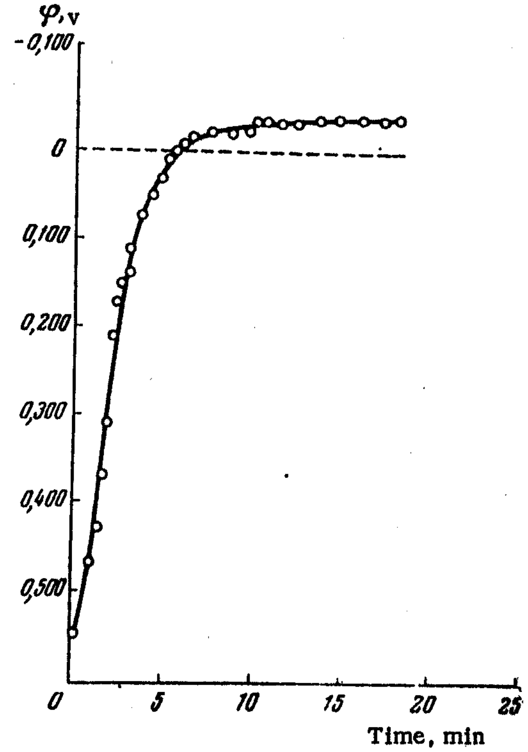

Fig. 1. The effect of atomic hydrogen on the potential of nickel in 1 N NaOH without the passage of an electric current.

The main experimental difficulty was the creation on the electrode of sufficiently thin layers of solution that hydrogen atoms entering it were unable to react with each other. According to the work of Harteck and Stewart [2] complete recombination of hydrogen atoms occurs even when they penetrate a solution to a depth of $1 \cdot 10^{-4}$ cm. We solved the problem of creating extremely thin layers of solution by forcing the gas mixture through the liquid in the form of bubbles onto the electrode surface. Nickel and mercury electrodes were mainly used for the study.

Figure 1 shows the effect of atomic hydrogen on the potential of nickel in 1 N NaOH without the passage of an electric current. Time in minutes is plotted along the abscissa axis and the electrode potential in volts relative to a reversible hydrogen electrode along the ordinate. As the curve (Fig. 1) shows, at the beginning of the experiment the electrode potential was 550 mv more positive than the hydrogen electrode. Under the action of H atoms, the potential of nickel was gradually displaced in a negative direction and, after 20 min., it reached a value of 45 mv more negative than a reversible hydrogen electrode. In a number of experiments we obtained even greater displacements of the potential in a negative direction (up to 70 mv).

In an alkaline medium nickel is known to be capable of functioning as a hydrogen electrode under normal conditions, i. e., with saturation of the solution with molecular hydrogen. The introduction of H atoms

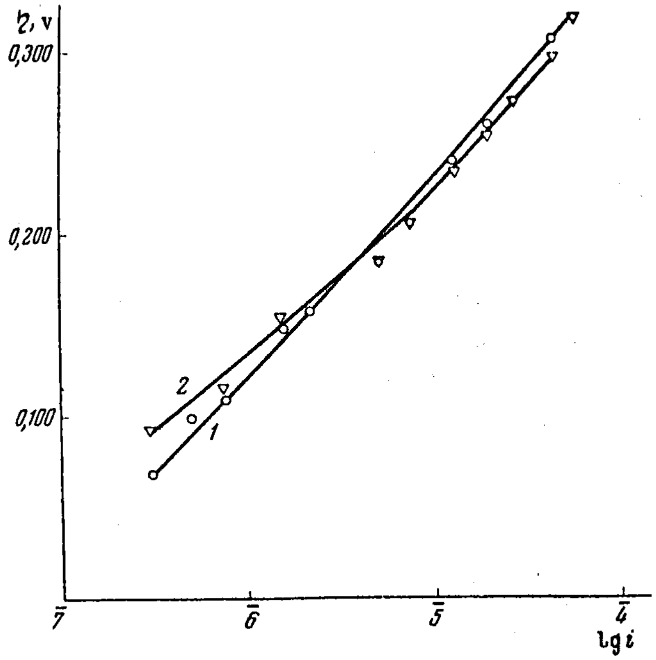

Fig. 2. Hydrogen overvoltage in relation to logarithm of current density (on nickel). 1) In the absence of atomic hydrogen; 2) in the presence of atomic hydrogen.

from a foreign source into the gas medium is accompanied by their ionization on the nickel surface according to the reaction:

$$H_{ads} + OH^- = H_2O + e, \qquad (1)$$

which produces a displacement of the nickel potential in a negative direction. When the flow of H atoms was stopped, the nickel potential moved back in a positive direction. Figure 2 shows the relation between the hydrogen overvoltage and the logarithm of the current density both in the presence of atomic hydrogen (curve 2) and without it (curve 1). The curves were plotted over a comparatively large range of current densities (10^{-7}–10^{-4} a/cm^2). Figure 2 shows that curves 1 and 2 intersect and at low polarizing current densities the passage of H atoms again produced a slight displacement of potential in a negative direction. In the upper part of the curves there was a slight fall in the overvoltage in the order of 5 - 6 mv.

From this we can draw the following conclusions. Reaction (1), i. e., the ionization of hydrogen at low overvoltages, proceeds on nickel at an appreciable rate and affects the electrode potential. In the region of high overvoltages, the ionization of atomic hydrogen is so slow that its effect becomes inappreciable. As regards the fall in overvoltage, though it was very slight, it was repeated in most of our observations and therefore it may be regarded as a quite real result. An experiment with nickel poisoned with mercury showed even more clearly the fall in overvoltage under the action of H atoms (Fig. 3). Curve 2 was obtained in the presence of H atoms. The coincidence of the curves in the upper points is probably explained by the fact that in this region the amount of free atoms coming from outside was small in comparison with the current passed.

Thus, on nickel, in addition to the "reducing" action of hydrogen atoms in the region of low overvoltages, there is a slight "oxidizing" action in the region of high overvoltages.

Such an "oxidizing" action of atomic hydrogen may be explained by the fact that the removal of hydrogen from the electrode occurs by the mechanism of "electrochemical desorption," as has already been proposed by a number of authors. This mechanism is based on the fact that hydrogen molecules are formed not due to the combination of two atoms on the cathode but as a result of the interaction of a hydrogen atom on the electrode surface, with a hydrogen ion from the solution if the electrolyte is acid (a) and a water molecule with an alkaline electrolyte (b), according to the schemes:

$$\text{a)}\ H_{ads} + H_3O^+ + e = H_2 + H_2O; \qquad (2)$$

$$\text{b)}\ H_{ads} + H_2O + e = H_2 + OH^-. \qquad (3)$$

As A. N. Frumkin [3] showed, the mechanism of "electrochemical desorption" may be used to explain processes occurring on electrodes with a low overvoltage. This mechanism would also occur in such systems as mercury in acid as the discharge of hydrogen atoms by their combination in molecules is improbable due to their very low concentration at the surface. The additional introduction of hydrogen atoms naturally should accelerate reactions (2) and (3) and displace the potential toward more positive values, as is observed in experiment.

A mechanism similar to "electrochemical desorption" was proposed by Horiuti and Okamoto [4], who postulated the possibility of the formation of the molecular ion H_2^+ on the cathode. This ion should also have an

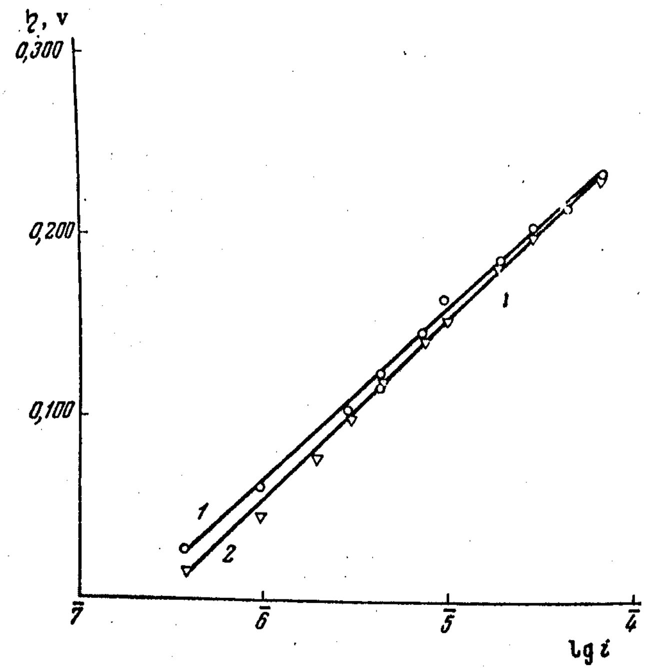

Fig. 3. Hydrogen overvoltage in relation to the logarithm of the current density (on nickel poisoned with mercury). 1) In the absence of atomic hydrogen; 2) in the presence of atomic hydrogen.

"oxidizing" action and displace the potential of the cathode in a positive direction. However, as is shown by the latest published work [5], these authors have not yet been able to confirm experimentally the existence of H_2^+. Weiss [6] studied the action of ultraviolet rays on acid solutions of divalent iron and explained the observed oxidation of iron by the action of the molecular ion H_2^+. Weiss used the presence of this ion to explain processes occurring in solutions under the action of radiation [7].

At the very beginning of our investigation, experiments were carried out with mercury in acid [8] in which a fall in overvoltage under the action of H atoms was also observed. However, we do not consider it possible to discuss these results yet as they were obtained by another method, which is less reliable than the one we use at the present time.

The work presented in this report is the beginning of an investigation of both the "reducing" and "oxidizing" properties of hydrogen on electrodes.

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