HYDROGEN-ISOTOPE SEPARATION FACTOR AND MECHANISM OF THE ELEMENTARY ACT

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We have shown that for a mercury cathode the potential dependence of S, the hydrogen-isotope separation factor, which is different for different solutions, is the same if S is expressed as a function of the potential jump in the dense part of the double layer, i.e., as a function of the field acting directly on the ions. This circumstance permits an experiment to choose between two mechanisms for the elementary discharge act: activation by stretching of the covalent O — H bond (according to Horiuchi and Polyani [1]) and activation by reorganization of the solvent without a change in the O — H bond (according to Dogonadze, Kuznetsov, and Levich [2]). For the first mechanism, when we take the possibility of the tunnel effect into account (see, e.g., [3]), the value of S should be the same for different metals with potential barriers of the same shape, i.e., in a first approximation, when the difference between the energies of the initial and final states is the same. For the second mechanism, the change in the magnitude of S with the potential can only be related to a change in the degree of overlap of the proton wave functions in H_3O^+ and M — H, due to a change in the distance between the ion and the electrode, i.e., due to a change in the field acting on the ion.

We measured the value of S for protium and tritium on gallium in 1 N H_2SO_4, and compared the results with the analogous data for mercury. The values of S for these cathodes are different at the same overvoltage. Comparison at identical elementary-act energies (i.e., at roughly the same potential barrier) greatly increases the discrepancy, while comparison at an identical potential jump in the dense part of the double layer (at an identical surface charge, according to the data of [4]) shows the S values to be close for the different cathodes. Accordingly, data on the separation factor contradict the hypothesized stretching of the O — H bond during activation.

LITERATURE CITED

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