MECHANISM FOR REMOVAL OF HYDROGEN ATOMS FORMED DURING BARRIER-FREE DISCHARGE OF HYDRONIUM IONS

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In examinations of the removal of hydrogen atoms from the surface of an electrode at high cathodic potentials, the ionization reactions are usually neglected, because the rate constant for these reactions decreases exponentially with an increase in the cathodic overvoltage, and turns out to be rather small. This simplification, however, is not suitable for barrier-free hydrogen ion discharge—in this case the ionization is activation-free; i.e., its rate constant is maximally high and is independent of potential [1, 2].

A more detailed examination of the methods of hydrogen removal during a barrier-free discharge was therefore of interest.

In the steady state, the rate of H atom formation (1) is equal to the rate of their removal by the ionization reaction (2) and electrochemical desorption (3)*

$$k_1x(1-\theta) = k_2(1-x)\theta + k_3x\theta. \tag{1}$$

Here k_i are the corresponding rate constants (they may in principle depend on the potential), θ is the partial surface coverage by adsorbed hydrogen, x is the mole fraction of hydrogen ions in the double layer, and 1-x is the same quantity for water molecules (we neglect the presence of other ions—they will have no effect on the end results).

A barrier-free process is possible only during a strongly endothermic discharge act (for mercury, in particular, at the equilibrium potential, ΔH kcal [2, 3]. Consequently electrochemical desorption at these electrodes must occur extremely exothermically, and its activation energy must tend to zero. Actually, the magnitude of the standard barrier $E_0^{\neq}$, i.e., the activation energy when there is no thermal effect on the elementary act*, can be estimated on the basis of data on the hydrogen overvoltage on strongly hydrogen-adsorbing metals, for which slow electrochemical desorption is the most probable (the hydrogen adsorption energy is unknown for them). Such an estimate yields an $E_0^{\neq}$ of about 2 kcal [1, 5]. With a transfer coefficient of $\alpha = 1/2$, a sufficient difference in the energy levels to reduce this barrier to zero is about 4 kcal. It is then beyond doubt that, even when all possible errors in the estimate of $E_0^{\neq}$, are taken into account the electrochemical desorption of hydrogen from a mercury cathode is activation-free.

For two activation-free processes—ionization and electrochemical desorption—the rate constants are equal [1]. Hence it follows that only a fraction $x/(1+x) \ll 1$, of the total amount of discharging hydrogen is converted into molecular hydrogen, while the greater part of formed atoms is converted back into hydrogen ions. Assuming that the total current flowing, i, is twice the electrochemical desorption current, and finding from (1) the steady-state value of θ, we obtain:

$$i = 2k_3x\theta = 2\frac{k_1k_3x^2}{k_3 + k_1x} \simeq 2k_1x^2. \tag{2}$$

Here k_i depends exponentially on the potential. The second order of the reaction with respect to hydrogen ions follows from Eq. (2) (at constant potential; if a constant overvoltage is maintained, k_i turns out to be inversely

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* As usual we neglect the rate of reversible electrochemical desorption, because at high cathodic potentials it cannot be activation-free for the cathode under study (see below).

† In our previous papers we called this energy the "universal activation energy" [1, 4, 5].

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proportional to x, and the overall order will be first). Experiment, however, in sharp contradiction with this result, shows a first order with respect to H_3O^+ (zeroth order at constant overvoltage) [1, 2].[*] This discrepancy with experiment can be removed if one considers the possibility of yet another means of hydrogen removal—electrochemical desorption, but with the participation of water molecules, rather than hydronium ions (we denote the corresponding rate constant by k_4):

$$H_{ads} + H_2O + e^- \rightarrow H_2 + OH^-.$$

The Eq. (1) is replaced by

$$k_1x(1-\theta) = k_2(1-x)\theta + k_3x\theta + k_4(1-x)\theta. \tag{3}$$

In the reaction in which the water molecules participate, the difference in the levels of the initial and final states is smaller than in the reaction in which the hydronium ions participate, by the heat of neutralization of H_3O^+ ions by OH^- ions, equal to 13.5 kcal (this is easy to show from the equations for the corresponding reactions). The real heat of electrochemical desorption in which the hydrogen ion participates amounts to 22 kcal (heat of formation); it is thus 8.5 kcal for the corresponding reaction with the water molecule. This value is completely sufficient to decrease the activation barrier for electrochemical desorption to zero. If one takes into account that the experimental data mentioned above refer to a cathodic overvoltage greater than 0.3 V, when the level of the initial state is increased by 7 kcal and more, then it becomes certain that under these conditions the electrochemical desorption occurs activation-free with the discharge of water. Hence it follows that $k_2 = k_3 = k_4$ and that a fraction $1/(2-x)$, i.e., a little more than half of the hydrogen atoms formed during discharge, is subsequently removed in the form of H_2, and somewhat less than half ionizes to form H_3O^+ ions again. Each H atom formed has practically equal probabilities for desorption in the form of H_2 or ionization, returning to its initial state. Expressing the initial partial surface coverage θ by (3), we obtain

$$i = 2[k_3x + k_4(1-x)]\theta = \frac{2[k_3x + k_4(1-x)]k_1x}{(k_2+k_4)(1-x) + k_3x + k_1x} \simeq k_1x \tag{4}$$

Thus the total current turns out to be practically equal to the current for barrier-free discharge, corresponding to first order with respect to hydrogen ions at constant potential (i.e., to zeroth order at constant overvoltage). This result is in complete agreement with experiment. In a similar manner one can show that the current is independent of the ψ_1-potential.

Thus the proposition, based on energy considerations, of an activation-free electrochemical desorption of hydrogen in which water molecules participate is in good agreement with kinetic data on the removal of hydrogen from a mercury cathode. The magnitudes of the corresponding thermal effects for a silver cathode are noticeably smaller [6], and it is therefore difficult to reach on the basis of these effects, a reliable conclusion about the possible activation-free course of electrochemical desorption with discharge of water[*]. The nature of the kinetic dependences on this cathode, however, is similar to that on mercury [8, 9], so that it is extremely probable that in this case also there is an important participation of water molecules in the electrochemical removal of hydrogen.

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[*] Strictly speaking, yet another conclusion follows from (2) which is contradicted by experiment—the dependence of the overall rate on the ψ_1-potential (the barrier-free discharge rate does not depend on it [1, 2], but the rate of activation-free desorption is determined by the surface concentration of H_3O^+, which depends in the magnitude of ψ_1). It should be taken into account, however, that with a very large reaction rate constant one can hardly consider the concentration of hydrogen ions near an adsorbed hydrogen atom to be equilibrium. Here a kinetic calculation of the steady-state value of the concentration, based on the equality of the rate of ion disappearance due to electrochemical desorption and the rate of the supply from the bulk solution, is probably necessary. The latter rate may turn out to depend only on the bulk concentration.

[†] The results of the calculation depend on the estimate of the height of the standard barrier, the differences in the energy levels of adsorbed hydrogen near an H_3O^+, ion or an H_2O^- molecule, the heat of adsorption of water, and that of the ions. Similar effects were discussed in relation to the question of the transition from slow discharge of H_2O to a prevailing discharge.

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