2. C. J. Brockmann, Electroorganic Chemistry, Wiley, New York (1926) [Russian translation: ONTI-Khimteoret. Leningrad (1937)].
3. W. German Patent 1101436 (1961).
4. Austral. Patent 556166 (1953).
5. U.S. Patent 3195468 (1968).
6. U.S. Patent 3663381 (1972).
7. German Patent 117129 (1900).
8. U.S. Patent 557166 (1943).
9. U.S. Patent 3616324 (1973).
10. U.S. Patent 3616323 (1973).
11. British Patent 430572 (1935).
12. Tr. Mosk. Khimiko-Tekhnol. Inst., No. 32, 115 (1961) [Physical Chemistry and Electrochemistry].
13. G. A. Kakhanov and L. M. Yakimenko, USSR Inventor's Certificate 289823, Byul. Izobret., No. 2 (1971).

BARRIERLESS DISCHARGE OF HYDROGEN IONS

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It had been shown previously that at sufficiently low overvoltages, hydrogen evolution at mercury and silver cathodes follows the laws of slow, barrierless discharge characterized by a value $\alpha = 1$, a Tafel slope of 2.3 RT/F, and an overvoltage which is independent of hydrogen ion concentration and double-layer structure (cf. the review [1]). It was pointed out in [2] that the same slope will be found in slow, activationless electrochemical desorption ($\alpha_2 = 0$) preceded by quasi-equilibrium discharge. This mechanism was rejected since desorption involving H_3O^+ leads to a substantial dependence of reaction rate on hydrogen ion concentration and ψ' potential. It was shown subsequently, however, that from energy considerations, activationless electrochemical desorption involving water molecules is very likely [3]. If activationless desorption involving H_2O is slow, while the discharge is practically reversible, then the overvoltage must be found to be independent of H_3O^+ ion concentration and double-layer structure, i.e., the kinetic laws for such a mechanism are indistinguishable from those of slow, barrierless H_3O^+ ion discharge.

Let us examine the energy profile of the process involving barrierless discharge (transition 1-2, Fig. 1) and activationless electrochemical desorption (transition 2-3). Let us assume at first that the highest apparent activation energy (E) corresponds to the rate-determining step of the process. Then it can be seen that electrochemical desorption following rate-determining barrierless discharge must be activationless (for otherwise, when the final state is described by term 3', the rate-determining step would be electrochemical desorption: $E' > E$). Similarly, activationless rate-determining electrochemical desorption must be preceded by barrierless discharge. Thus, with the assumption made, and regardless of which step will be the rate-determining step, an experimental value $\alpha = 1$ always is associated with barrierless (or quasi-barrierless, cf. below) discharge.*

In discharge of heavy particles, the energy profile depicted in Fig. 1 will correspond, not to two consecutive steps but to a single two-electron transition from state 1 into state 3, while state 2 will be the activated reaction complex rather than any independent, relatively stable state of the system. But for a proton transfer reaction, state 2 may exist over a certain period of time, since the transition from one term to the other is accomplished, not each time when the point of intersection of the terms is reached but only in the

*Here the earlier conclusions regarding the energy of activation, the heat of the elementary act of discharge (with the corresponding correction for quasi-barrierless discharge), and the entropy of the process [1, 4] remain valid.

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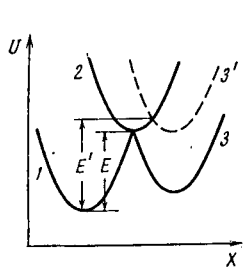

Fig. 1

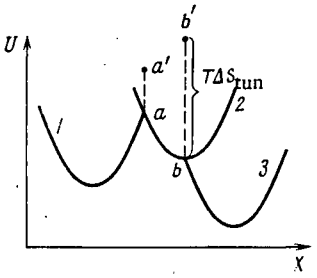

Fig. 2

Fig. 1. The energy profile of the hydrogen evolution reaction when the possibility of proton tunnelling is disregarded. The transition from term 1 to term 2 corresponds to the discharge step $H_3O^+ + e \rightarrow H_a + H_2O$; that from term 2 to term 3 (or 3') corresponds to the electrochemical desorption steps $H_a + H_3O^+ e \rightarrow H_2 + H_2O$ or $H_a + H_2O + e \rightarrow H_2 + OH$.

Fig. 2. The energy profile of the hydrogen evolution reaction when an entropy term with proton tunnelling probability different from unity (ΔS_{tun}) is taken into account. Notation is the same as in Fig. 1.

relatively rare instances governed by the tunnelling probability of the proton. Therefore the process occurs as a sequence of two steps, and from state 2 the system can pass into the final state 3 (the H_2 molecule) and also return to the initial state. Hence for hydrogen ion discharge, the sequence barrierless discharge–activationless desorption is made possible by modern quantum mechanical theory [5, 6]. The problem thus arises to select the slow step among the two consecutive steps: barrierless discharge or activationless desorption involving H_2O.*

Usually preference has been given to the first mechanism, since in the region of high overvoltages, the desorption rate constant undoubtedly is higher than the discharge rate constant, while at lower overvoltages, because $\alpha_1 > 0$ and $\alpha_2 = 0$, this correlation should not change unless in the transition point from $\alpha_1 = 1/2$ to $\alpha_1 = 1$ there is a discontinuous rate change (e.g., because of increasing preexponential factor). In this last case a polarization curve of complicated shape ought to be expected, which is not found experimentally [7]. Keeping in mind, however, that various effects could accidentally compensate, it was desirable to find an independent way of choosing between the two mechanisms.

This selection can be made on the basis of the data of [8, 9] where it was shown by the photoemission technique that activationless ($\alpha_2 = 0$) electrochemical desorption and activationless ($\beta_1 = 0$) hydrogen ionization do exist. It was also shown in [8] that on mercury cathodes, water molecules are the predominating proton donor in electrochemical desorption up to an acidity of about 0.01 M, and H_3O^+ ions are the proton donor in more acidic solutions. Thus, even though both processes are activationless (or quasi-activationless), the rate constants for desorption involving H_3O^+ are substantially larger (approximately by a factor of 5×10^3).†

Since $\alpha_2 = 0$ for both reactions, their relative rates should be substantially independent of potential; one thus can assume that even at lower potentials than those studied in [8], desorption via H_3O^+ prevails in acidic

*A strong difference in the tunnelling probabilities can in principle lead to the situation where the first step is reversible, ordinary discharge while the rate-determining step is activationless electrochemical desorption. In this case the highest point of the potential energy profile (cf., Fig. 2) no longer determines the energy of activation, since the entropy factor (the tunnelling probability) causes point a to be higher than point b on the profile of standard free energy (compare a' and b').

†The large difference between these constants can be explained by the closer approach of the H_3O^+ ions to the electrode, which facilitates tunnelling [10]. A difference of the same order of magnitude was found for the preexponential factor in the ordinary discharge of H_3O^+ ions and H_2O molecules [11]. When these processes are quasi-activationless, then the difference between the rate constants can also be attributed to different values of their activation energies (these are independent of potential).

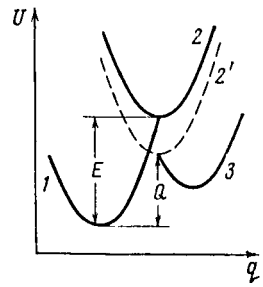

Fig. 3. The energy profile of the quasi-barrierless hydrogen evolution reaction. Notation is the same as in Fig. 1.

solutions (there may be a change in the relative rates with decreasing potential owing to a transition from $\alpha_2 = 0$ to $\alpha_2 = 1/2$, but this transition ought to set in earlier for the reaction involving H_2O, which is energetically less favorable; i.e., the pH range over which desorption via H_3O^+ will prevail can only become wider). In the photoemission experiments, adsorbed hydrogen is produced by another route than during H_3O^+ discharge, so that its energy state can be different; it is most likely that it has higher energy. Therefore one hardly can expect complete agreement between the rate constants of electrochemical desorption in these two cases. As one goes over to the ordinary electrochemical process (which is equivalent to lowering the energy of hydrogen), the change of α_2 from 0 to 1/2 will come about more rapidly for the reaction with H_2O molecules. Thus, if under the conditions of the photoelectrochemical experiments electrochemical desorption involving H_3O^+ was predominant, then it will also be predominant in electrochemical experiments.

The data on barrierless discharge [1] referred to hydrogen ion concentrations of the order of 0.1 to 1.0 M, i.e., notoriously to the region of pH where H_3O^+ ions are the predominant proton donor. Therefore independence of overvoltage on pH proves unambiguously that barrierless discharge but not the electrochemical desorption is slow.

Slow barrierless discharge with fast, activationless desorption involving H_3O^+ means that activationless ionization (the transition 2-1 in Fig. 1) will occur with a significantly lower probability than activationless desorption (the transition 2-3). This difference could be explained by a large difference in the tunnelling probabilities of these two processes. Another mechanism leading to the same result is quasi-barrierless discharge.

Quasi-barrierless and quasi-activationless processes had been predicted in [12, 13] as the result of two types of motion during an electrode reaction: solvent reorganization and displacement of the discharging species. The existence of quasi-barrierless and quasi-activationless processes had recently been demonstrated experimentally for the discharge and ionization of chlorine on ruthenium–titanium oxide electrodes [14].

The discharge of proton donors in principle is also associated with the displacement of heavy particles, since the equilibrium positions of the oxygen atoms relative to the electrode in pairs H_3O^+–H_2O and H_2O–OH^- in all probability are different, owing to the different forces of interaction of ions and neutral molecules with the electrode [10, 11].

According to these ideas, the quasi-barrierless discharge of hydrogen ions can be represented by the scheme shown in Fig. 3. The system passes from state 1 into state 2: barrierless discharge along the q coordinate, as a result of solvent reorganization (reaction coordinate q) with practically unchanged position of the center of gravity of the H_3O^+ ions. With the discharge completed and the proton severed from H_3O^+, the H_2O molecule produced is too close to the electrode, and owing to the significant repulsion forces it rapidly relaxes into a new equilibrium position (state 2'). The potential dependence of the activation energy is determined by terms 1 and 2, but the value of activation energy E differs from the heat Q of the elementary act which corresponds to equilibrium values of all coordinates by the energy difference between the minima of terms 2 and 2', i.e., by exactly the excess energy residing in the water molecule immediately after proton separation.

The inverse process, ionization, requires the water molecules first to approach the electrode, for which an energy of activation which is constant and potential-independent is used. Thus, a perceptible activational barrier stands in the way of the back reaction; the reaction turns out to be quasi-activationless ($\beta = 0$ for the transition from term 2 to term 1). This stabilizes state 2, and provides the time for the H_3O^+ ion to approach the adsorbed H atom; this H_3O^+ ion then accomplishes activationless electrochemical desorption (the transition 2'-3).

LITERATURE CITED

1. L. I. Krishtalik, Usp. Khim., 34, 1831 (1965).
2. L. I. Krishtalik, Zh. Fiz. Khim., 33, 1715 (1959).
3. L. I. Krishtalik, Élektrokhimiya, 4, 877 (1968).
4. L. I. Kirshtalik, Élektrokhimiya, 5, 3 (1969).
5. R. R. Dogonadze and A. M. Kuznetsov, Itogi Nauki, Élektrokhimiya 1967 [Progress in Science. Electrochemistry 1967], VINITI, Moscow (1969), p. 5.
6. R. R. Dogonadze and A. M. Kuznetsov, Itogi Nauki, Fiz. Khimiya, Kinetika [Progress in Science, Physical Chemistry, Kinetics], Vol. 2, VINITI, Moscow (1973).
7. L. I. Krishtalik, Élektrokhimiya, 10, 1862 (1974).
8. V. I. Lakomov, Z. A. Rotenberg, and Yu. V. Pleskov, Élektrokhimiya, 6, 515 (1970).
9. Yu. A. Prishchepa, Z. A. Rotenberg, and Yu. V. Pleskov, J. Electroanal. Chem., 66, 3 (1975).
10. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 5, 1501 (1969); 9, 810 (1973); L. I. Krishtalik and V. M. (Tsionsky), J. Electroanal. Chem., 31, 363 (1971).
11. E. N. Potapova, L. I. Krishtalik, and I. A. Bagotskaya, Élektrokhimiya, 10, 53 (1974).
12. L. I. Krishtalik, J. Electroanal. Chem., 21, 421 (1969); Élektrokhimiya, 6, 507 (1970).
13. A. M. Kuznetsov, Élektrokhimiya, 5, 479, 742 (1969).
14. R. G. Érenburg, L. I. Krishtalik, and I. P. Yaroshevskaya, Élektrokhimiya, 11, 1068, 1072, 1236 (1975).

KINETICS OF SILVER OXIDE DISSOLUTION IN ALKALI SOLUTION

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The silver oxide electrode is characterized by high energy capacity and low solubility at high discharge rates, so that it is used in silver–zinc and silver–cadmium power sources, both in one-shot applications and under conditions of prolonged reversible operation. The electrochemical behavior of the silver oxide electrode in power sources is largely governed by the kinetics of the reduction processes. At the different stages this process can occur, both via a solid-phase mechanism and by a mechanism presupposing the intermediate dissolution of the metal ions. It will depend on the solubility of the oxides and their electronic conductivity whether one or the other mechanism is realized [1, 2]. The cathodic reduction of silver oxide via the electronic mechanism is favored by the relatively low bond energy between the oxygen atom and the metal and the much higher conductivity of silver as compared to the starting oxide [3-5]. On the other hand, the relatively high solubility of silver oxide in strong alkaline solutions (10^{-4} M) makes a process via the solution feasible [6-8].

The task was set in the present work to investigate the kinetics of silver oxide dissolution in 1 N KOH solution, more precisely, to measure the rate of AgO dissolution and to determine how this depends on the rate of rotation of the electrode.

To measure the rate of silver oxide dissolution we used the method suggested in [9], viz., a rotating disk of the oxide being examined in conjunction with a ring electrode in order to determine the concentration of silver ions.

An integral silver electrode with a disk diameter of 2.9 mm and a silver ring was used in the work. The silver was 99.99 grade. The electrode was mounted in Teflon the spacer between disk and ring electrode was of fluoroplast [polytetrafluoroethylene]. The butt end of the electrode was polished with carborundum or sand paper having a grain size of 5 μm. In 1 N KOH solution a mercury–mercuric oxide electrode in the same alkali solution was

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