HYDROGEN OVERVOLTAGE ON SILVER AT LOW CURRENT DENSITIES.

II. TEMPERATURE DEPENDENCE OF THE PROCESS RATE

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UDC 541.13

Study of the temperature dependence of the rate of an electrochemical process is an important method for study of its nature and mechanism. In those cases in which the hydrogen evolution rate is determined by an electrochemical step, the actual activation energy can be determined from the experimental data [1] – from the temperature dependence of the current at constant overvoltage. It is connected with the latter by

$$A = A_0 - \alpha\eta F, \tag{1}$$

where A_0 is the actual activation energy at the equilibrium potential. The temperature dependence of hydrogen evolution on silver has practically not been studied up till now.* This process, as we showed earlier [3], occurs by a barrier-free mechanism in a certain range of potentials on silver. The activation energy of a barrier-free process offers the possibility of finding the Ag-H bond adsorption energy, the magnitude of which has not yet been determined. A determination of the hydrogen-metal bond energy would allow a more complete description of the cathodic process.

METHOD

The experimental preparation and procedure are described in detail in [3]. Measurements were conducted in solutions of 0.1 N sulfuric and 0.1 N hydrochloric acid. A series of polarization curves for various temperatures were obtained in the following manner: the first curve was recorded at 25°C, then temperature measurements were performed at some constant current density, and a new curve was recorded after the establishment of a constant potential at the new temperature, etc. At the end of the series, measurements were again conducted at 25°C. The agreement of curves at the beginning and end of the series served as proof that the change in overvoltage was a result of a change in temperature only. Each series of curves was taken on one electrode. Similar series of curves were obtained in the temperature range 10-25°C. Similar measurements at higher temperatures could not be made, for the increase of temperature to 40-60°C noticeably decreased the overvoltage, but upon returning to 25°C the curves did not coincide; consequently the surface of the electrode underwent some kind of change during the temperature increase. In connection with this, the linear dependence between log i and 1/T was always disturbed in these experiments. The temperature dependence of the electrode reaction rate was also determined by the change in the overvoltage at constant current density in the moderate temperature range (22-28°C).

EXPERIMENTAL RESULTS

Typical series of curves obtained in solutions of sulfuric and hydrochloric acid are shown in Figs. 1 and 2. The real activation energy A was determined from the slope of the log i vs. 1/T curve at constant overvoltage.† This overvoltage was chosen so that the curves at all temperatures were located within the barrier-free region. Several curves of log i vs. 1/T are shown in Fig. 3. The good maintenance of a linear dependence is seen in Fig. 3. The values of the activation energy found at a given overvoltage were corrected to the equilibrium potential; i.e., to $\eta = 0$ in Eq. (1). The preexponential factor in the equation

* There are polarization curves for evolution of hydrogen on silver in the temperature range 25-60°C in [2]. These results were not discussed, however, and there is no information in the paper on the method of studying the temperature dependence. Our treatment of these data showed that they do not conform to a linear dependence of log i on 1/T. Apparently an irreversible change in the composition of the surface occurred with the increase in temperature during the experiments of [2]; we observed a similar phenomenon (see below).

† The activation energy determined is the so-called apparent activation energy; it does not include a component associated with the H_3O^+ adsorption energy, for the comparison of log i at the various temperatures is made at a constant H_3O^+ concentration in the bulk solution, not at the electrode surface.

Electrochemistry Institute, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 4, No. 2, pp. 233-237, February, 1968. Original article submitted January 2, 1967.

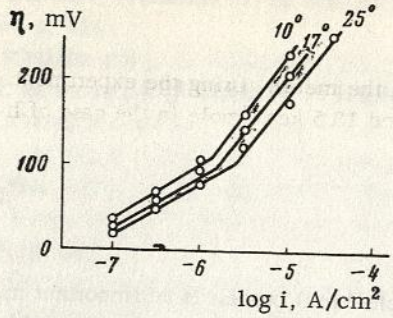

Fig. 1. Polarization curve in 0.1 N H_2SO_4 at various temperatures. Curves at 25°C at the beginning and end of the series coincide.

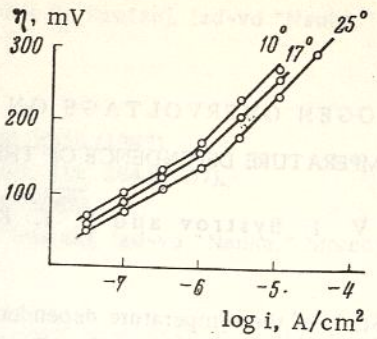

Fig. 2. Polarization curves in 0.1 N HCl at various temperatures. Curves at 25°C at the beginning and end of the series coincide.

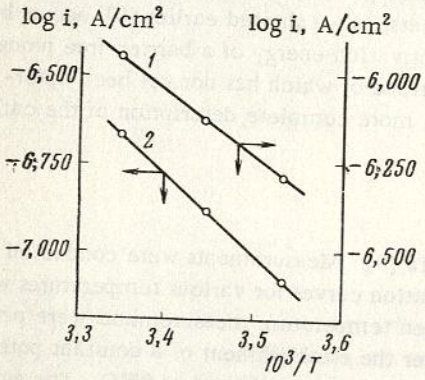

Fig. 3. Temperature dependence of the process rate: 1) in 0.1 N H_2SO_4; 2) in 0.1 N HCl.

$$i_\eta = ke^{-A\eta/RT} \tag{2}$$

was also determined from the log i vs. 1/T curves. The activation energy was found from the change in overvoltage at constant current density in the moderate temperature range from the equation

$$A = -TE\left(\frac{\partial \eta}{\partial T}\right). \tag{3}$$

The values so determined are shown in Table 1.

DISCUSSION OF RESULTS

As was shown in [3], a barrier-free process, namely a barrier-free slow discharge, occurs during the evolution of hydrogen on silver in a certain range of potentials. In this case the kinetics of hydrogen evolution are determined by the step

$$H_3O^+ + e^- \rightarrow H_a + H_2O_{surf}.$$

The barrier-free process occurs when the activation energy of the reverse reaction – in this case ionization – is equal to zero. Hence it follows that the activation energy for the barrier-free reaction is equal to the energy of the elementary act. Quantitatively this relation is expressed by the following equation [4, 5]

$$A = -R\left(\frac{\partial \ln i}{\partial 1/T}\right)_\eta = \Delta H_{a_{H_2O}} + \Delta H_{a_H} - \eta F + RT \tag{4}$$

or, at the equilibrium potential,

$$A_0 = \Delta H_{a_{H_2O}} + \Delta H_{a_H} + RT. \tag{5}$$

TABLE 1

Expt. No.	Solution comp., 0.1 N	A_η = 100 mV	A_η, kcal per mole	log k	Expt. No.	Solution comp., 0.1 N	A_η = 100 mV	A_η, kcal per mole	log k
1	H_2SO_4	8,05	10,35	−0,457	5	HCl	11,0	13,3	1,39
2	H_2SO_4	8,50	10,80	0,07	6	HCl	11,0	13,3	1,41
3	H_2SO_4	8,55	10,85	0,35	7	HCl	10,6	12,9	0,85
		avg. 8,37	10,67	−0,13	8	HCl	10,8	13,1	0,90
4 *	H_2SO_4	9,2 *	10,50	−0,2			avg. 10,85	13,15	1,16

* The activation energy was determined from the temperature coefficient at 25°C and log i = −7.0. The value A_η corresponds to η = 59 mV.

The enthalpy of water adsorption, i.e., the change in enthalpy during the transfer of a mole of water from the bulk solution to the double layer, enters Eq. (5). This was estimated to have the value ~ -1.0 kcal/mole for mercury in similar calculations [5]. There is no reason for assuming a significant change for silver, since the question here is of water in contact with adsorbed hydrogen atoms, not directly with the metal. Using the experimental values of A_0, we find ΔH_{0H} in the case of sulfuric acid to be 11.0 kcal/mole, and 13.5 kcal/mole in the case of hydrochloric acid. Knowing the heat of adsorption of hydrogen and its heat of dissociation [6], one can find the Ag-H bond adsorption energy. It turns out to be 41 kcal/mole during hydrogen evolution from sulfuric acid solutions and 38 kcal/mole from hydrochloric acid solutions.

As the above account shows, the Ag-H bond adsorption energy is less than the heat of dissociation of H_2; therefore the buildup of a large amount of adsorbed hydrogen on silver is energetically unfavorable. This conclusion is in good agreement with the fact that adsorption of hydrogen from the gaseous phase on silver has not been observed experimentally [7]. If the slow step were barrier-free electrochemical desorption, the activation energies we found would correspond to essentially exothermic adsorption of hydrogen: the bond energy would amount to 63-66 kcal, i.e., about the same as on platinum group metals. In this case silver would have to strongly adsorb hydrogen and show a high adsorption capacitance. These conclusions are in sharp contradiction with experimental results.

The only mechanism, then, which is in quantitative agreement with all the experimental information is the mechanism of a slow barrier-free discharge of hydrogen ions.

Measurements of the temperature dependence in solutions of various compositions show the effect of a specific adsorption of anions on the magnitude of the Ag-H bond energy. Thus, in the case of the more strongly adsorbed chloride ion, the adsorption energy of the bond is 3 kcal smaller than that determined in the sulfuric acid solution. A lowering of the adsorption energy of the Me-H bond in the case of specific adsorption of halides is observed on many metals; in particular, there are quantitative results for platinum in which a lowering of the Pt-H bond energy in HCl solutions by 3 kcal with respect to H_2SO_4 solutions of the same concentration is observed [8].

During the evolution of hydrogen on silver this slight difference in the Ag-H bond energy in solutions of various concentrations does not change the nature of the process or the slow step, as is evident from the very similar kinetic behaviors [3]. In speaking of the absence of a noticeable hydrogen adsorption, we have in mind a picture of that part of the metallic surface on which the reaction is mainly occurring. It is for this silver surface that we are determining the process rate, its temperature dependence, and consequently the bond energy. There may, however, be other adsorption centers on the electrode, with higher bond energies, which are practically filled under our experimental conditions, and have practically no effect of the kinetics of the process. As Leikis and Aleksandrova have shown [9], discharge at these centers can be studied with the aid of an alternating current of sufficiently high frequency.

We were interested in the relation of our data to the theory of emission removal of hydrogen atoms from the electrode surface [10]. If one eliminates the contradictory assumptions of this theory discussed in [11], the emission of hydrogen must be described in the following manner. The emission rate, in electrical units, is

$$i = k \cdot \theta e^{-E/RT}. \tag{6}$$

Here k is the preexponential factor, E is the energy of activation for emission, equal in the first approximation to the bond energy of the metal with adsorbed hydrogen. The degree of filling θ with current due to the (assumed in the theory of slow emission) equilibrium of adsorbed hydrogen with H_3O^+ ion in the solution is determined to be

$$\theta = \theta_0 e^{\eta F/RT}. \tag{7}$$

where θ_0 is the degree of filling at the equilibrium potential. The latter is equal to

$$\theta_0 = k' e^{-\Delta H_H^{\alpha}/RT} = k' e^{-(\Delta H_H - E)/RT}. \tag{8}$$

Here $\Delta H_{\alpha H}$ is the energy of adsorption of an H atom from gaseous hydrogen. It can be found from the energy of formation of a free H atom (ΔH_H) and the energy of its bond with the metallic surface. Substituting Eqs. (7) and (8) into Eq. (6), we get

$$i = k'' e^{-\Delta H_H/RT} e^{\eta F/RT}. \tag{9}$$

A similar equation was obtained in [11]. From it follows independence of the overvoltage of the nature of the metal, and a polarization curve slope equal to 59 mV. This situation served in [11] as grounds for rejection of the assumption that the emission mechanism has any real meaning.

It should be noted that Eq. (9) at first glance describes our data well – that obtained for mercury [12] and silver [3], both with respect to the slope of the polarization curve, and with respect to the independence of the overvoltage of the solution composition. Equation (9) is, however, in sharp contradiction with the data on the activation energy of the process. For mercury, the value A_0 = 22.9 kcal was found earlier [5], and the value A_0 = 13.1 kcal was found in the present paper for silver, while according to Eq. (9), this value should be equal to ΔH_H, i.e., 52 kcal. We note that the single assumption made in the derivation of Eq. (9) – the equality of the emission activation energy to the adsorption bond energy – in all probability lowers the theoretical activation energy, i.e., the corresponding correction only worsens the agreement with experiment. An additional argument against the emission mechanism is that the overvoltages on mercury and silver are significantly different – the difference is greater than 0.3 V – for the same slope of about 60 mV. According to the emission mechanism they should be the same. Thus the data on the activation energy and the dependence of the overvoltage on the electrode material unambigusously refute the possibility of an explanation by the slow emission of adsorbed hydrogen atoms of the phenomena we observed.

The values of the preexponential factor obtained in this study are smaller than in the case of barrier-free discharge on hydrogen ions on mercury (log k = 3.0) and smaller than the theoretical values calculated from absolute rate theory [4]. The dependence of this quantity on the nature of the metal and the large disagreement with theory are evidence of the inaccuracy of absolute rate theory as applied to the cathodic evolution of hydrogen.

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