INFLUENCE OF THE pH OF THE SOLUTION ON THE ADSORPTION OF HYDROGEN AND OXYGEN ON PLATINUM AND RHODIUM ELECTRODES

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UDC 541.135.5-183

A study of the dependence of the adsorption of hydrogen and oxygen on the pH of the solution permits conclusions to be drawn on the state of adsorbed atoms on the electrode surface. As was first shown in [1], from acid to alkaline solutions the amount of hydrogen A_H adsorbed on a Pt/Pt electrode increases at low and medium degrees of coverage of the surface with H_{ads} and decreases at high degrees of coverage. The observed dependence is explained by the presence of two types of $Pt-H_{ads}$ dipoles: at low degrees of coverage the dipoles are turned with the negative end toward the solution, while at high degrees of coverage they are turned with the positive end toward the solution. The amount of adsorbed oxygen A_O, according to the data of [1], increases with increasing pH at low degrees of coverage. According to [2, 3], at all potentials on rhodium A_H increases with increasing pH. In [4] it was shown on the basis of the dependence of A_H on the pH found in [2] that the dipole of hydrogen on rhodium is turned with the negative end toward the solution, and its contribution to the potential drop is substantially greater than on platinum. These conclusions were confirmed in [5] by another method. However, it should be mentioned that the dependence of the adsorption of hydrogen and oxygen on the pH on platinum was determined in [1] only in the transition from acid to alkaline solutions. The method of analyzing the data used in [2, 3] to determine the dependence of A_H on the pH on rhodium is approximate. Therefore, a further study of the influence of the pH on the adsorption of hydrogen and oxygen is advisable.

In this work we consider the influence of the pH on the adsorption of hydrogen and oxygen in the following systems: Pt/Pt electrode in $H_2SO_4 + 1$ N Na_2SO_4 (pH 1.60-3.74), HCl + 1 N KCl (pH 1.20-3.34), HBr + 1 N KBr (pH 1.15-3.15) and rhodium-plated electrode in $H_2SO_4 + 1$ N Na_2SO_4 (pH 1.67-3.74). The preparation of the electrodes and determination of their true surface were described in [6]. The potentials φ are related to the reversible hydrogen electrode in the same solution. The experiments were conducted at 20 ± 1°C.

The A_H versus φ_r curves were determined in the following way. The charging curves relating to other pH for the systems studied were constructed from the equilibrium charging curves [7] in solutions of 0.01 N H_2SO_4 + 1 N Na_2SO_4, 0.01 N HCl + 1 N KCl and 0.01 N HBr + 1 N KBr, using the isoelectric shifts of the potential [6-8]. Then according to the equation

$$A_H = \Gamma_{H^+} - Q, \tag{1}$$

where Q is the total charge of the surface, while Γ_{H^+} is the free charge [9], we calculated the A_H versus φ_r curves. The Γ_{H^+} versus φ curves at various pH, obtained earlier [6], were used for the calculation.

The construction of the A_H versus φ_r curves on a rhodium electrode and the A_H versus φ_r curves in the other investigated systems are shown in Figs. 1 and 2. The dependences of $(\partial A_H/\partial \mu_{H^+})_{\varphi_r}$ on φ_r, which are cited in Fig. 3, were calculated according to the data of Figs. 1 and 2.

In acidified chloride and bromide solutions the A_H versus φ_r curves at anodic potentials have a vertical portion corresponding to $A_H = 0$ [7-9]. In sulfate solutions, as a result of overlapping of the regions of adsorption of hydrogen and oxygen, there is no such portion [10]. At $\varphi_r \simeq 0.12$ and 0.4 V on Pt and 0.22 V on Rh, in these cases, intersections of the A_H versus φ_r curves $[(\partial A_H/\partial \mu_{H^+})_{\varphi_r} = 0]$, relating to different pH are observed. In order to

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M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 6, No. 3, pp. 404-407, March, 1970. Original article submitted July 30, 1969.

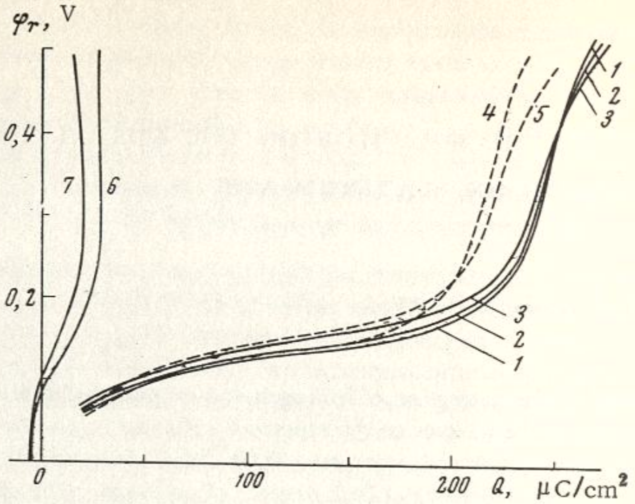

Fig. 1. Charging curves (1-3), A_H versus φ_r curves (4, 5), and adsorption curves (6, 7) on a rhodium electrode in 0.01 N H_2SO_4 + 1 N Na_2SO_4 at various pH: 1, 4, 6) 1.67; 2) 2.3; 3) 5, 7) 3.74.

understand the factors leading to such phenomena, let us consider the question of the influence of pH on the adsorption of hydrogen and oxygen from the standpoint of thermodynamic theory.

From Eqs. (10) and (10a) of [1], it is easy to obtain the function

$$(\partial A_H/\partial \mu_{H^+})_{\varphi_r} = \frac{X}{X+Y}(\partial A_H/\partial \varphi_r)_{\mu_{H^+}}, \tag{2}$$

where μ_{H^+} is the chemical potential of hydrogen ions; X is the contribution of the atom and Y the contribution of the ion to the potential drop [1, 5]. Similar functions were considered earlier in [2, 3]. Since $d\varphi_r = -(1/2)d\log p_{H_2}$, where p_{H_2} is the partial pressure of hydrogen in the system, the dependence of the adsorption of hydrogen on the pH at p_{H_2} = const is determined by the shape of the isotherm of the adsorption of hydrogen and the ratio of the contributions of the atom and ion to the potential drop. The derivative $(\partial A_H/\partial \varphi_r)_{\mu_{H^+}} < 0$, $Y > 0$, and $Y > X$ [1, 5]. Consequently, the sign of $(\partial A_H/\partial \mu_{H^+})_{\varphi_r}$ is determined by the sign of X. The amount of adsorbed hydrogen at constant φ_r increases with increasing pH, i.e., $(\partial A_H/\partial \mu_{H^+})_{\varphi_r} < 0$, if $X > 0$. The condition $X > 0$ means that the $Pt-H_{ads}$ dipole is turned with the negative end toward the solution. In the case of orientation of the dipole with the positive end toward the solution, $X < 0$, while $(\partial A_H/\partial \mu_{H^+})_{\varphi_r} > 0$, i.e., the amount of adsorbed hydrogen drops with increasing pH at φ_r = const.

According to Eq. (2), the amount of adsorbed hydrogen does not depend on the pH in those cases when X = 0 or $(\partial A_H/\partial \varphi_r)\mu^{H^+} = 0$. The latter can be observed only when complete coverage of the surface with H_{ads} is reached and in the absence of adsorbed hydrogen on the electrode.

Thus, evidently the points of intersection of the A_H versus φ_r curves of platinum and rhodium in sulfate solutions correspond to the potentials at which X = 0. At φ_r = 0.12 V on platinum, X becomes zero as a result of compensation for the charges at the potential drop, due to the dipoles of hydrogen of different orientation [1-5]. At φ_r = 0.4 V on platinum and 0.22 V on rhodium, X and, consequently $(\partial A_H/\partial \mu_{H^+})_{\varphi_r}$ become zero as a result of the appearance of adsorbed oxygen. Since $\Delta A_H = -\Delta A_o$ [1, 5], then $(\partial A_H/\partial \mu_{H^+})_{\varphi_r} = -(\partial A_o/\partial \mu_{H^+})_{\varphi_r}$. Thus, the indicated potentials correspond to a state of the surface in which the summary contributions of hydrogen and oxygen atoms are the same in sign and absolute magnitude. Since in general the contribution of the atom H_{ads} and the contribution of the atom O_{ads} differ in magnitude, obviously the amounts of the adsorbed hydrogen and oxygen atoms may be different at these potentials.

The negative value of $(\partial A_o/\partial \mu_{H^+})_{\varphi_r}$, found experimentally, means that the dipole of the adsorbed oxygen is turned with the negative end toward the solution. This agrees with the data on the influence of the adsorption of anions on the adsorption of oxygen on platinum and rhodium [11] and with the result of the calculation in [5].

As follows from Fig. 3, the influence of pH on the adsorption of hydrogen depends on φ_r, the nature of the metal, and the composition of the solution. The greatest influence of the pH is observed on a rhodium electrode.

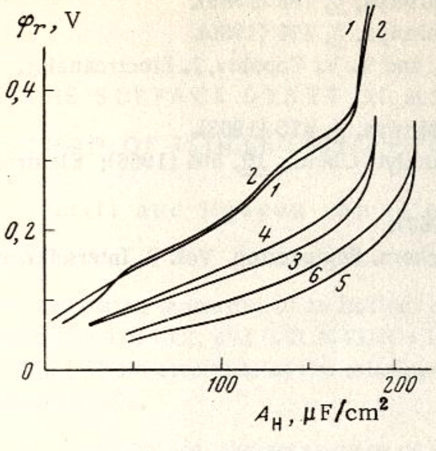

Fig. 2

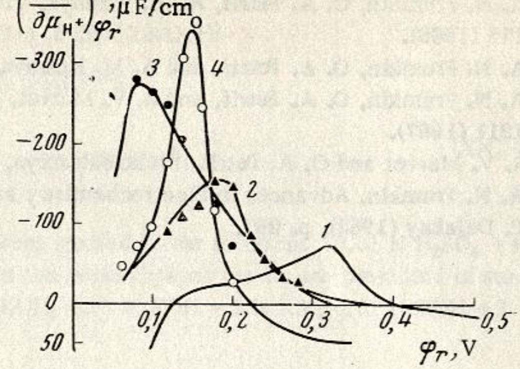

Fig. 3

Fig. 2. A_H versus φ_r curves of a platinized platinum electrode in acidified sulfate (1, 2), chloride (3, 4), and bromide (5, 6) solutions at pH: 1) 1.6; 2) 3.74, 3) 1.2, 4) 3.34, 5) 1.15, 6) 3.15.

Fig. 3. Influence of the pH of the solution on the adsorption of hydrogen on platinum (1-3) and rhodium (4) in acidified sulfate (1, 4), chloride (2), and bromide (3) solutions.

Evidently the difference in the behavior of Pt and Rh is associated with the presence of two types of adsorbed dipoles of hydrogen on Pt, the influence of the pH on the adsorption of which is opposite in sign. On platinum the dependence of A_H on the pH increases along the series $SO_4^{2-} < Cl^- < Br^-$.

The dependence of A_H upon the pH that we found on rhodium differs from the data of [2, 3], according to which $(\partial A_H/\partial\mu_{H^+})_{\varphi_r}$ = const at medium degrees of coverage of the surface with adsorbed hydrogen. Evidently, the cause should be sought in the different methods of treating the experimental data.

The dependence of $(\partial A_H/\partial\mu_{H^+})_{\varphi_r}$ on φ_r can be obtained not only from an analysis of the A_H versus φ_r curves. It can be calculated according to Eq. (2) from the values of X and Y found earlier [8] and the derivatives, $(\partial A_H/\partial\varphi_r)_{\mu_{H^+}}$, calculated according to the slope of the A_H versus φ_r curves. The results of such a calculation are shown by points in Fig. 3. The coincidence of the calculated and experimental $(\partial A_H/\partial\mu_{H^+})_{\varphi_r}$ versus φ_r curves is a natural consequence of the applicability of Gibbs thermodynamics to the systems under consideration, which was demonstrated earlier [7, 9].

Actually, if we express the ratio $X/X+Y$ with the aid of Eqs. (1) and (2) of [5], then function (2) of this article can be rewritten in the form

$$\frac{(\partial A_H/\partial\mu_{H^+})_{\varphi_r}}{(\partial A_H/\partial\varphi_r)_{\mu_{H^+}}} = -\frac{(\partial\Gamma_{H^+}/\partial\mu_{H^+})_{\varphi_r} - (\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}}}{(\partial Q/\partial\varphi_r)_{\mu_{H^+}} - (\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+}}}. \qquad (3)$$

Using Eq. (1) and performing simple transformations, function (3) is reduced to the equation

$$(\partial Q/\partial\mu_{H^+})_{\varphi_r} = (\partial\Gamma_{H^+}/\partial\varphi_r)_{\varphi_{H^+}}, \qquad (4)$$

which follows directly from the Gibbs adsorption equation [1, 4, 9].

Let us express our deep gratitude to Academician A. N. Frumkin for his valuable suggestions in the discussion of this work.

LITERATURE CITED

1. A. N. Frumkin and A. I. Shlygin, Izv. AN SSSR, Otd. Khim. Nauk, 773 (1936); Acta Physicochim. URSS, 5, 819 (1936).
2. Yu. M. Tyurin and A. M. Tsybulevskaya, Dokl. Akad. Nauk SSSR, 159, 1140 (1964).
3. Yu. M. Tyurin and A. M. Kossaya, Élektrokhimiya, 4, 103 (1968).
4. A. N. Frumkin, N. A. Balashova, and V. E. Kazarinov, J. Electrochem. Soc., 113, 1011 (1966).

5. O. A. Petrii, A. N. Frumkin, and Yu. G. Kotlov, Élektrokhimiya, 5, 735 (1969).
6. O. A. Petrii, A. N. Frumkin, and Yu. G. Kotlov, Élektrokhimiya, 5, 476 (1969).
7. A. N. Frumkin, O. A. Petrii, A. M. Kossaya, V. S. Éntina, and V. V. Topolev, J. Electroanalyt. Chem., 16, 175 (1968).
8. A. N. Frumkin, O. A. Petrii, and A. M. Kossaya, Élektrokhimiya, 4, 475 (1968).
9. A. N. Frumkin, O. A. Petrii, and R. V. Marvet, J. Electroanalyt. Chem., 12, 504 (1966); Élektrokhimiya, 3, 1311 (1967).
10. R. V. Marvet and O. A. Petrii, Élektrokhimiya, 3, 901 (1967).
11. A. N. Frumkin, Advances in Electrochemistry and Electrochem. Engineering, Vol. 3, Interscience Publ., Ed. P. Delahay (1963), p. 287.