STUDY OF THE ADSORPTION PROPERTIES OF RUTHENIUM AND PLATINORUTHENIUM ELECTRODES

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In [1-7] the thermodynamics of surface phenomena on metals of the platinum group was considered, and an experimental confirmation of the thermodynamic functions derived was cited. The following equation was verified:

$$\left(\frac{\partial \Gamma_{H+}}{\partial \varphi_r}\right)_{\mu_{H+},\mu_s} = \left(\frac{\partial \Gamma_H}{\partial \varphi_r}\right)_{\mu_{H+},\mu_s} \left(\frac{\partial \varphi_r}{\partial \mu_{H+}}\right)_{\Gamma_{H+},\mu_s}, \qquad (1)$$

where Γ_H and Γ_{H+} are the surface densities of hydrogen and hydrogen ions in the Gibbs sense; φ_r is the potential with respect to the reversible hydrogen electrode in the same solution; μ_{H^+} and μ_s are the chemical potentials of hydrogen ions and of the background electrolyte.

This work presents the results of a verification of the applicability of Eq. (1) to ruthenium and platinoruthenium electrodes.

The preparation of the Pt + Ru electrode (10% by weight Ru) was described in [8]. Ruthenium electrodes were deposited on a platinum grid from 0.1 N KOH with simultaneous dissolution of metallic ruthenium powder at the anode [9] at room temperature and at 80°C or from a solution of $H_2RuNOCl_5$ [8]. The visible surfaces of the electrodes comprised 20 and 80 cm^2. A verification was conducted at 20 ± 1°C for solutions of 0.01 N HCl + 1 N KCl and 0.01 N KOH + 1N KCl on Ru and 0.01 N HCl + 1 N KCl on a Pt + Ru electrode. The preliminary preparation of the electrodes included cathodic polarization in 1N H_2SO_4, prolonged washing with double-distilled water in air, and reduction with hydrogen in a measuring cell.

For the rest, the experimental procedure and treatment of the results were kept the same as in [4, 5].

Figure 1 presents the dependences of $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s} = \left(\frac{\partial \varphi_r}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s} + 1$ upon φ_r for Pt + Ru and Ru electrodes, in comparison with the data for a Pt/Pt electrode [4, 5]. The values of $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s}$ were determined by replacing a solution of 0.001 N HCl (or KOH) + 1.009 N KCl by a solution of 0.1 N HCl (or KOH) + 0.91 N KCl. As can be seen, the shape of the $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s}$, versus φ_r curves depends substantially upon the nature of the electrode. Thus, although in the case of a Pt/Pt electrode, $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s}$ becomes zero when $\varphi \le 0.45$ V, the minimum value of this quantity on a Pt + Ru electrode is equal to 0.3. For Ru in an acidified solution of KCl, the minimum value of $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s}$ is only 0.6, while in an alkalized solution of KCl, in the entire region of potentials, $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s}$ is close to one, i.e., the electrode behaves as a reversible hydrogen electrode, existing in equilibrium with gaseous hydrogen at constant pressure.

In accord with [2], the results obtained mean that in the case of Pt + Ru, just as especially in the case of a Ru electrode, the regions of adsorption of hydrogen and oxygen overlap even at high concentrations of Cl^- ions in solution. When $\varphi_r > 0.3$ V in acidified KCl and when $\varphi_r > 0.07$ and 0.52 V in an alkalized solution on Ru, $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s}$ becomes greater than one or $\left(\frac{\partial \varphi_r}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s} > 0$. Since $\left(\frac{\partial \Gamma_H}{\partial \varphi_r}\right)_{\mu_{H+},\mu_s} > 0$, this is evidence of the passage of the Γ_{H+} versus φ_r curves through maxima.

The values of $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s}$ presented in Fig. 1 were obtained on a Ru electrode that had worked for some time in chloride solutions. On freshly prepared electrodes, $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s}$ are poorly reproducible when $\varphi_r < 0.35$ V; moreover, especially substantial changes are observed at potentials of the transition from $\left(\frac{\partial \varphi}{\partial \mu_{H+}}\right)_{\Gamma_H,\mu_s} < 1$ to

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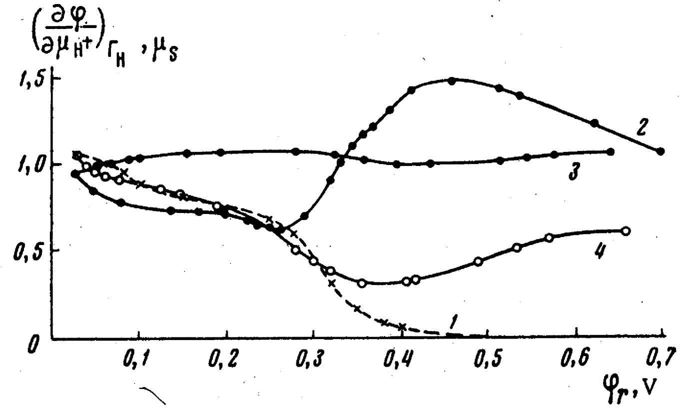

Fig. 1. Dependence of $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_H, \mu_s}$ upon φ_r on Pt/Pt (according to the data of [4, 5])–1; Ru–2; and Pt + Ru–4 in a solution of 0.01 N HCl + 1 N KCl and on Ru–3 in a solution of 0.01 N KOH + 1 N KCl.

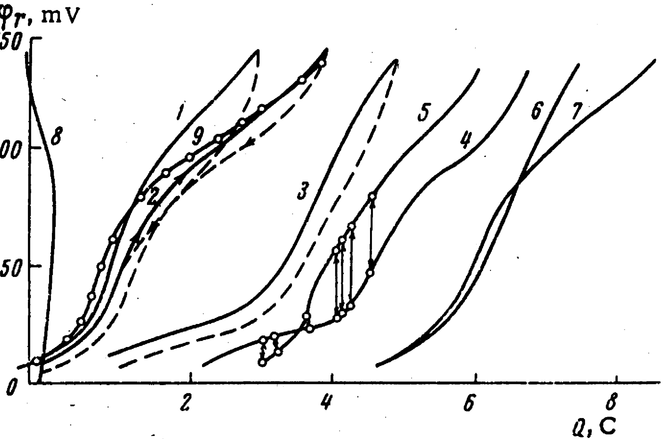

Fig. 2. Charging curves (dotted line–cathodic curves) on ruthenium electrodes: 1) in 1 N KCl + 0.01 N HCl; 2) equilibrium curve in the same solution; 3) in 1 N KCl + 0.01 N KOH on an electrode that had worked for a long time in alkaline solution; 5) in 1 N KCl + 0.01 N HCl on an electrode that had worked for a long time in alkaline solution; 6) in 1 N H_2SO_4 on an electrode freshly prepared from a nitrosochloride solution; 7) in 1 N H_2SO_4 on an electrode freshly prepared according to the method of [9]; 8) adsorption curve of Ru in 1 N KCl + 0.01 N HCl; 9) A_H versus φ_r curve in 1 N KCl + 0.01 N HCl. The arrows connect the points corresponding to Γ_H = const in acidified and alkalized solutions.

$\left(\frac{\partial\varphi}{\partial\mu_{H^+}}\right)_{\Gamma_H, \mu_s} > 1$. Evidently these phenomena are due to the peculiarities of the chemisorption of oxygen on Ru,* in particular, changes in the nature of the oxidation of the surface during conditioning of the catalyst.

The slow charging curves on Ru electrodes in alkaline solution and on Pt + Ru electrodes, measured by the usual method, are sufficiently reversible. However, in an acidified solution of KCl on Ru, an appreciably hysteresis was observed between the anodic and cathodic charging curves (Fig. 2), which introduces an indeterminacy into the

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* In the case of prolonged operation of a Ru electrode (especially in alkaline solution), a certain change in the shape of the charging curve is observed, evidently due to the same factors (Fig. 2). In addition, the shape of the charging curves of Ru in the oxygen region in 1 N H_2SO_4 differs for electrodes prepared from a solution of the nitrosochloride and according to the method of [9]. However, in the presence of substantial Cl^- concentrations, these differences disappear, while the values of $(\partial\varphi_r/\partial\mu_{H^+})_{\Gamma_H, \mu_s}$ are practically the same on different electrodes.

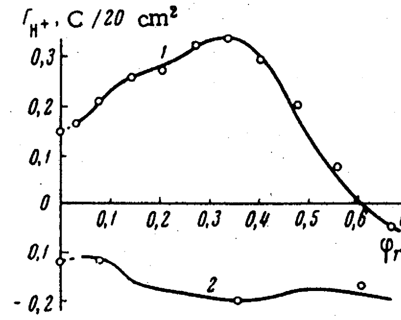

Fig. 3. Dependence of Γ_{H^+} upon φ_r on a Ru electrode: 1) in 1 N KCl + 0.01 N HCl and 2) in 1 N KCl + 0.01 N KOH, calculated theoretically (solid curve) and found experimentally (points).

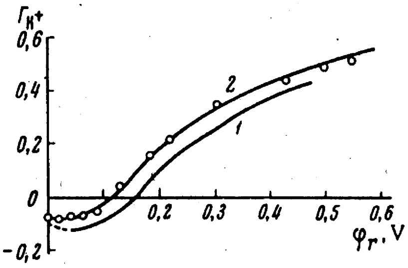

Fig. 4. Dependence of Γ_{H^+} upon φ_r in 1 N KCl + 0.01 N HCl on a Pt/Pt electrode (according to the data of [4, 5]) (1) and on a Pt + Ru electrode (2), calculated theoretically (solid curve) and found experimentally (points).

determination of the values of $\left(\frac{\partial\Gamma_H}{\partial\varphi_r}\right)_{\mu_{H^+},\mu_s}$, required for calculation according to Eq. (1). Therefore, the charging curves were measured in the following way. A certain amount of electricity was communicated to the electrode, after which polarization was stopped and was resumed only after the establishment of a constant value of the potential. The values of φ_r established when the circuit was opened were plotted as a function of the amount of electricity passed through. The anodic and cathodic shapes of such curves, arbitrarily called equilibrium, coincide at the adsorption potentials of hydrogen, while at the adsorption potentials of oxygen (up to 0.7 V), they exhibit only a small hysteresis (Fig. 2), since the selection of the direction of change of the potential during the measurement of the charging curve has little effect upon the calculation of the Γ_{H^+} versus φ_r curves.* The anodic curves were used for the calculations.

From Figs. 3 and 4 it follows that the theoretically calculated and experimental Γ_{H^+} versus φ_r curves coincide quantitatively both on Pt + Ru and on Ru electrodes. This result demonstrates the possibility of considering the electrodes studied as equilibrium systems, the state of which at μ_s = const is determined by the independent variables μ_H and μ_{H^+} or μ_{OH^-}.

According to the Γ_{H^+} versus φ_r curves, the appearance of adsorbed oxygen on the Ru surface produces a drop in the adsorption of anions.† In alkaline solution, the surface of Ru is negatively charged in the entire region of potentials studied; moreover, the magnitude of the charge changes only negligibly. Analogous phenomena were noted earlier on a Pt/Pt electrode [1, 11, 12].

On Ru in an acidified solution of KCl at $\varphi_r = 0$, an adsorption of acid is observed, i.e., the point of zero charge lies at substantial cathodic potentials. The intersection of the x-axis with the Γ_{H^+} versus φ_r curve on Ru occurs only at $\varphi_r \approx 0.62$ V, which can be considered as the point of zero charge of oxidized Ru. The point of zero charge on the Pt + Ru alloy lies at 0.11 V, i.e., is shifted by 60 mV in the cathodic direction in comparison with the point of zero charge of platinum under the same conditions.

As was first detected in [9], the extent of the charging curve of Ru in alkaline solution is substantially greater than in acid solution. To clarify the question of whether the cause of the lengthening of the curve lies in an earlier deposition of oxygen in alkali or whether there is a simultaneous increase in the adsorption of hydrogen at $\varphi_r = 0$, we conducted experiments studying the change in the potential from 0.01 N HCl + 1 N KCl to 0.01 N KOH + 1 N KCl (or vice versa) under isoelectric conditions, i.e., when Γ_H = const. The results of these experiments, presented in Fig. 2, show that the charging curve in one of the solutions and the values of the shift of φ_r with changing pH can be used as the basis for constructing the charging curve in a different solution. This is an additional confirmation of the conclusion of reversibility of the systems studied. At $\varphi_r < 120$ mV, the replacement of an acid solution by an alkaline solution leads to an increase in φ_r, while at $\varphi_r > 120$ mV, it leads to a decrease in it. The results obtained can be interpreted, if we assume that in the transition to alkaline solutions there is both an earlier deposi-

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* The measurement of the charging curve by this method in one direction within the interval 0.04-0.7 V required 25-30 h.

† It should be mentioned that the adsorption curve that we obtained for Ru at anodic potentials differs from that described in the literature [10].

tion of oxygen and an increase in the adsorption of hydrogen at $\varphi_r = 0$. The appearance of the first portions of adsorbed oxygen in alkali can already be expected at $\varphi_r \sim 0.1$ V. However, for an exact estimation of the ratio of the amounts of adsorbed hydrogen in oxygen and alkali, the data obtained in this work are insufficient, which is due to the overlapping of the regions of adsorption of hydrogen and oxygen in the solutions studied. The results of a determination of the A_H versus φ_r curves according to the equation $\Gamma_H = A_H - \Gamma_{H^+}$, where A_H is the amount of adsorbed hydrogen in electrical units (Fig. 2), agree with the conclusion of overlapping of the regions of adsorption of hydrogen and oxygen. On the A_H versus φ_r curves, both in acidified and in alkalized solutions, no vertical portion corresponding to $A_H = 0$ is observed [1, 5, 6]. These circumstances must be taken into consideration when charging curves are used to determine the true surfaces of ruthenium catalysts.

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