ADSORPTION OF HYDROGEN ON PLATINUM OF DIFFERENT DEGREES OF DISPERSION

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The results of measurements of charge curves on smooth platinum, platinized platinum, platinum black, skeletal platinum and Adam's platinum are discussed. The influence of foreign contaminants on the shape of the charge curves and the potentiostatic curves for smooth platinum in sulfuric acid is shown.

In the present communication, results are discussed of measurements of charge curves and potentiostatic curves on different varieties of platinum catalyst. The charge curves on platinized platinum and platinum black were compared previously in the literature [1-4] and it was concluded that there was qualitative agreement in the type of curves in both cases. However, the obtained data for powdered electrodes did not possess sufficient accuracy for carrying out a quantitative comparison because there was observed a hysteresis between the anodic and cathodic curves during measurements in several cases [1, 2, 4].

As was shown first in [5], on the charge curve for a Pt/Pt electrode in sufluric acid, there is observed a step at about $\varphi_r \sim 600$ mV, which has been called the "central" step. In the case of measurements of potentiostatic curves, the indicated step must correspond to the maximum in the current in the same region of potentials. During discussions of the nature of the step, ideas have been put forward of strong adsorption of hydrogen [6, 7] or oxygen [8] on the surface of platinum, or of ionization of the hydrogen dissolved in the platinum at the potentials of the step [1, 4, 9, 10]. The step on the charge curve or the maximum on the potentiostatic curve was observed by several investigators also in solutions of phosphoric acid [11]. According to [6], it is possible to obtain "anomalous" platinum electrodes, on which a considerable portion of the adsorbed hydrogen is desorbed at $\varphi_r \sim 600$ mV. We made an attempt to clear up the nature of the "central" step and to reproduce the "anomalous" electrodes.

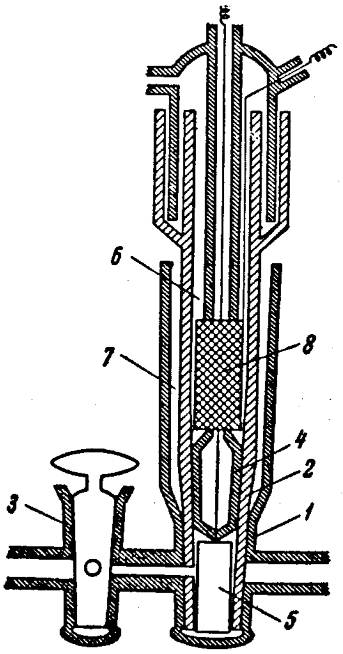

Fig. 1. Central part of the cell for measuring on smooth platinum: 1) container; 2) section; 3) valve; 4) internal section; 5) smooth platinum electrode; 6) space for purifications of solution; 7) filling section; 8) Pt/Pt grid (30 cm^2).

Method of Measurement and Preparation of Electrodes

We used in the investigation the methods of charge curves and slow potentiostatic runs. The method of measurements of the Pt/Pt electrode and the construction of the electrolytic cell were described in detail in [12]. This cell was used also in the experiments with the powdered catalyst. For the measurements on smooth platinum, another cell was used similar to the cell of Ershler [13], without the gaseous phase of the electrolyte and with a minimum quantity of electrolyte in the chamber of the operating electrode (about 0.5 cm^3/cm^2 surface of electrode). Part of the cell is shown in Fig. 1. In the container of the cell 1 there is a section 2 with a side opening which covers the inlet to the auxiliary and hydrogen electrodes. The latter is separated from the central part of the cell also by the value 3. In 2, from above is inserted in the section 4 the working electrode 5 in the form of platinum foil or grid coiled into a roll with a surface area of 30 cm^2. In the spaces 6 and 7, above the sections, is the electrolyte solution. In the space 6, is placed the Pt/Pt grid with an apparent surface area of 30 cm^2 for purification of the working solution. During purification of the solution, the section 4 is raised.

Stirring is achieved by periodic raising and lowering of the section 4. Space 6 is covered from above with a water seal. The total quantity of solution in the working portion and in 6 is about 2.5 mliter. The dissolved oxygen is removed

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Specific Surface Areas of the Electrodes (m^2/g)

Electrode	Freshly prepared	Aged
Pt-Skeletal (alloy with Al)	40	15
Pt/Pt	20—25	12
Adam's Pt	24	12,5
Pt Black	19	10,5
Pt-Skeletal (alloy with Li)	12	7

from the cell by cathodic polarization with a current of decreasing strength. The charge curves were measured with current densities of $I = 0.33\text{-}10\ \mu amp/cm^2$. The recording of the slow charge curves was carried out manually and the rapid ones with the help of an electrometric amplifier U-2 with recording on an electronic self-recording potentiometer ÉPP-09. For the measurements of the potentiostatic curves, the potentiostat TsLA PE-5611 was used. During this, with the aim of avoiding considerable ohmic drops of potential, the section 2 was established in such a way that the opening in it coincided with a side branch leading to the reference electrode. The potential φ_r was measured relative to a reversible hydrogen electrode in the same solution at the temperature of the experiment.

In addition to smooth and platinized platinum, we investigated platinum black, skeletal platinum and Adam's platinum. The platinum black was prepared by the method [14] of reduction of chloroplatinic acid by formaldehyde in an alkaline solution. The skeletal platinum was prepared from [15] with fusion of platinum black with aluminium or dissolution of the platinum powder in molten lithium in an argon atmosphere. The platinum catalyst obtained in the latter case in its external appearance was similar to platinum black. The Adam's platinum was prepared by [16] with oxidation of chloroplatinic acid with sodium nitrate. The platinum dioxide was afterwards subjected to cathodic reduction. All the powdered catalysts were introduced into the measuring cell coiled in the platinum grid.

The specific surface areas of freshly prepared electrodes and electrodes "aged" after prolonged heating at 95°C and with $\varphi_r = 500$ mV, calculated from the adsorption of hydrogen [12], are given in the table.[*]

EXPERIMENTAL PROCEDURE AND DISCUSSION OF RESULTS

The charge curves and the adsroption isotherms for hydrogen at 20°C on various catalysts, calculated on the basis of the hypotheses given in work [12], are given in Fig. 2.[†] From the obtained data, the difference between the dispersed catalysts on the one hand and smooth platinum on the other is apparent. In spite of the difference in specific surface areas and in the methods of preparation, the adsorption isotherms on the dispersed catalysts to a first approximation are coincident and differ considerably from the adsorption isotherm for hydrogen on smooth platinum, especially in the region of adsorption of strongly bonded hydrogen. Thus, in addition to the development of the surface area of platinum, an increase in the percentage of centers with high energy for hydrogen bonds occurs.

A more detailed examination shows small differences in the adsorption isotherms for hydrogen on various dispersed catalysts. However, for catalysts with a strongly developed surface area, there is no sharply expressed dependence between the value of the true surface area and the quantity of strongly bonded hydrogen. In several cases, it may be connected with the conditions for preparation of the catalyst. Thus, the lower content on the surface of the skeletal platinum of centers with a high bond energy with the adsorbed hydrogen is possible, as a result of some deactivation of the catalyst during prolonged treatment of the Pt-Al alloy in concentrated alkali for removal of Al. During the preparation of platinum black, evidently there is a great influence by the heating of the solution after

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[*] In the literature the opinion is often given that Pt/Pt electrodes have a considerably smaller surface area than platinum black (see for example [17], p. 179). As can be seen from the data in the table, in actual fact the specific surface area of Pt/Pt electrodes, calculated from the weight of the precipitate, is similar to the surface area of platinum black and even can exceed it. In our experiments, on 1 cm^2 apparent surface area of electrode, we deposited not more than 5 mg platinum, which corresponds to an average thickness of deposit of several microns, during which there was observed approximate linear proportionality between the weight of the deposit and its true surface area.

[†] In solutions of H_2SO_4, it is difficult to determine with great accuracy the potential at which covering by the adsorbed hydrogen is zero. This however does not cause substantial changes in the form of the isotherm. We propose to return to the problem of determining the anodic end of the hydrogen region solutions of sulfuric acid later.

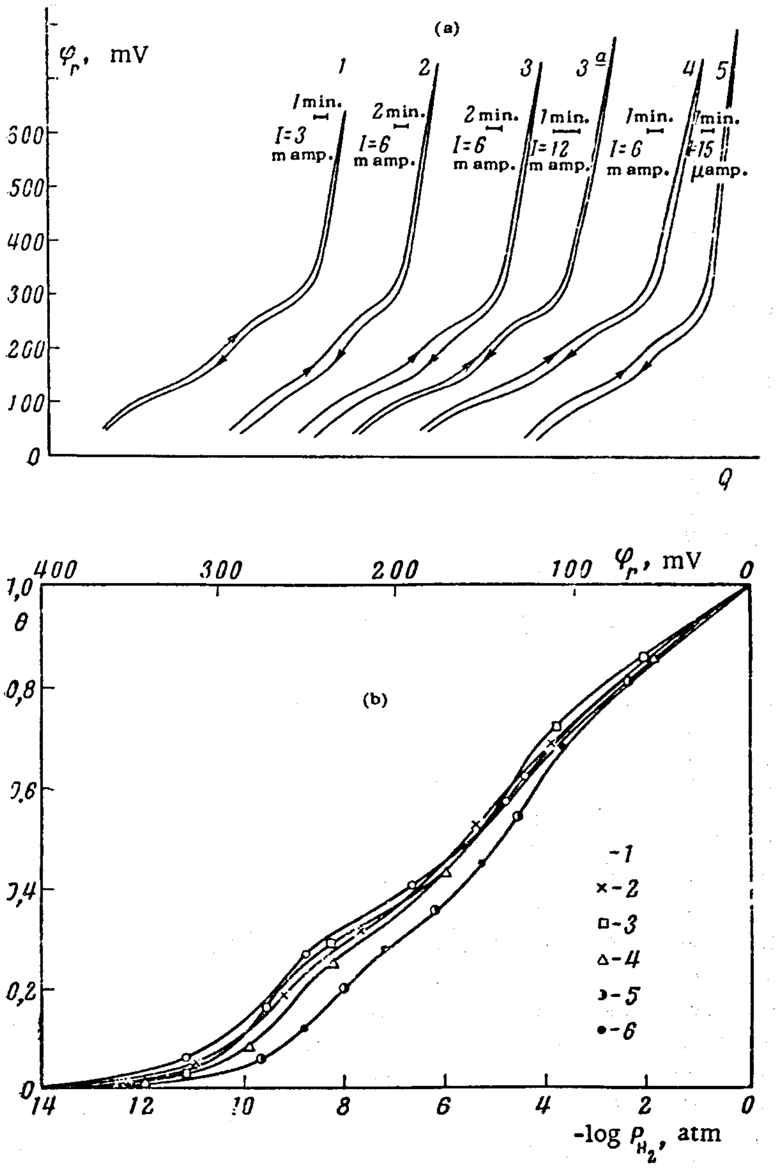

Fig. 2. Charge curves and adsorption isotherms for hydrogen on various platinum catalysts at 20°C in N H_2SO_4: 1) Pt/Pt (precipitated with a current of 2 m amp/cm^2); 2) skeletal platinum; 3) Adams platinum, prepared by cathodic reduction at 20°C; 3a) Adams platinum prepared by cathodic reduction at 95°C; 4) platinum black; 5) smooth platinum, i = 0.33 μamp/cm^2; 6) smooth platinum, i = 1.65 and 10 μamp/cm^2.

addition of sodium hydroxide to 60° (for coagulation of the deposit) which may deactivate the catalyst as was first observed by Taipale [18].

In addition to the small differences in the isotherms for hydrogen adsorption, there are also other peculiarities in the properties of the different catalysts. As can be seen from the table, after working at high temperatures (95°C, φ_r = 500 mV, 2-4 h) in all the samples of platinum, there is observed a marked decrease in surface area (about 50%). The greatest decrease is with skeletal platinum obtained from the Pt-Al alloy. During ageing of the electrodes, there is observed a change in the quantity of strongly bonded hydrogen. This phenomenon is observed on platinum black and skeletal platinum, but is especially strongly expressed on platinized platinum (Fig. 3).

From the samples shown above, the Adam's platinum stands out since after treatment at 95°C it retains a proportion of strongly and weakly bonded hydrogen characteristic for freshly prepared electrodes. In addition, these regions on the isotherm of the adsorption of Adam's platinum are much more sharply expressed than those of the other samples of platinum (Fig. 2). It should be noted that the sample of Pt-Adams obtained by reduction of platinum

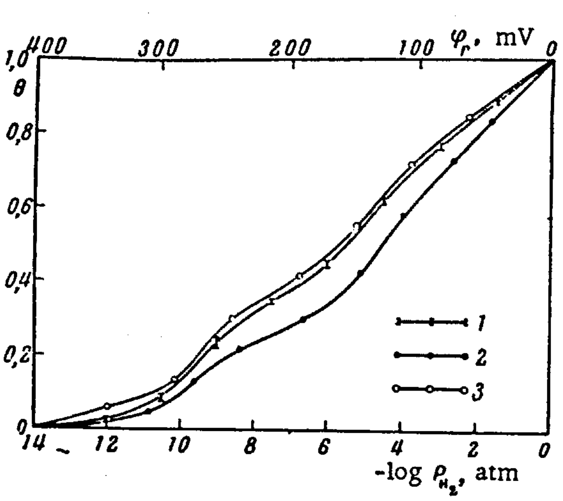

Fig. 3. Adsorption isotherms for hydrogen on Pt/Pt electrode precipitated with various current densities: 1) freshly prepared electrodes; vertical lines show the maximum difference in the isotherms on various electrodes; 2) after prolonged operation at 95°C; 3) electrode precipitated with a current of 200 m amp/cm^2 from a solution of 1% K_2PtCl_6.

oxide at 20°C has not such a sharply expressed transition between the regions of adsorption of the tightly and weakly bonded hydrogen (Fig. 2). Obviously, during an increase in temperature, there is a change in the structure of catalyst.

In contrast to the Pt/Pt electrode [12], a quantity of adsorbed hydrogen (in the limits of accuracy of the measurements) remains the same at all temperatures on the powdered catalysts. This difference is possibly explained by the structure of platinized Pt, in particular, by the presence of microcracks and channels between individual crystallites which are accessible for adsorption of hydrogen only at high temperatures [12].

On the studied samples of dispersed catalysts with a highly developed surface, we were not successful in observing a sharply expressed plateau in the double layer region in 1 and 0.1 N H_2SO_4. Therefore we investigated the influence of the conditions of platinization on the form of the charge curves. Electroprecipitation was carried out from solutions of 2% H_2PtCl_6 and 1% K_2PtCl_6 (chemically pure) at current densities from 1 to 200 m amp/cm^2. During platinization from solutions of H_2PtCl_6, precipitates are obtained with specific surface areas in the limits 20-25 m^2/g. The adsorption isotherms for hydrogen on the studied electrodes are shown in Fig. 3. During deposition of platinum at one and the same current density, good reproducible electrodes are obtained. Independent of current density and time of platinization, electrodes could be observed to any marked degree. Only in those cases when deposits were obtained of very small weight and low true surface area (about 0.55 mg/cm^2, roughness factor ≤40), did a small plateau in the double layer region appear on the charge curves and a maximum in the current on the potentiostatic curves. However, after purification of the solution in the operating part of the cells for adsorption on the large platinized grid by saturated hydrogen, the indicated plateau almost completely disappeared. After prolonged holding of the working electrode in purified solution at potentials in the hydrogen region, it again appeared. These experiments lead to the conclusion of the presence in the solutions of sulfuric acid of impurities which are adsorbed on the electrode and are oxidized at about 600 mV. It should be noted that the potential for the plateau agrees with the potentials for oxidation of various substances adsorbed on the surface of platinum, for example, alcohol [20], hydrocarbons [21-23], CO_2 [24] and so on. The presence of oxidizable impurities in the commercial preparations of sulfuric and phosphoric acids was shown in the work of Taker [25].

The absence of the plateaus in the solution of HCl* is obviously connected, on the one hand, with the fact that hydrochloric acid is more easy to purify and, on the other hand, with the strong retardation of the processes of adsorption and electrooxidation of organic substances in the presence of surface active anions† (see for example [26]).

We were not successful in obtaining the small plateaus at about 600 mV during platinization from a solution of 1% K_2PtCl_6, but these electrodes were not completely similar to the "anomalous" electrodes in [6]. During precipitation from a solution of potassium chloroplatinate, electrodes were obtained which had about 2 times less surface area than those precipitated from a solution of H_2PtCl_6. This was probably caused by the influence of the pH of the medium and possibly by the potassium ions on the conditions for electrodeposition. We observed that the addition of 0.5% KCl to the 2% H_2PtCl_6 results in the preparation of deposits, the charge curves of which are distorted and the quantity of strongly bonded hydrogen is small. On electrode precipitated from neutral solutions of K_2PtCl_6, the hydrogen adsorption isotherms are also somewhat different from the normal ones (Fig. 3).

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* In the work of Skopin [4] with powdered platinum catalysts, there was observed, after substituting in the cell a solution of H_2SO_4 with HCl the "central" plateau also in the latter. Evidently, in such an experiment there is a transfer of impurities into the solution of HCl.

† We showed that the "central" plateau in solutions of phosphoric acid was also caused by oxidizable impurities. Results of a study of the adsorption of hydrogen in solutions of phosphoric acid will be described in a separate communication.

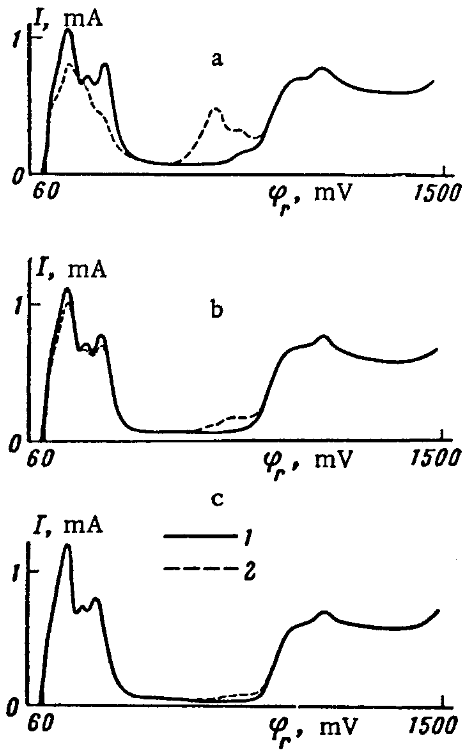

Fig. 4. Potentiostatic curves on smooth platinum in 1 N H_2SO_4: a) unpurified solution; b) particularly pure water, freshly distilled sulfuric acid; c) after additional purification of the preceeding solution by adsorption on a Pt/Pt grid; 1) periodic triangular sweep; 2) curves after holding the electrode for 30 min at 60 mV. Rate of sweep 18 mV/sec.

The conclusion about the role of oxidizable impurities in the formation of the "central" plateau* was confirmed by us by measurements of the charge curves and potentiostatic curves on smooth platinum. The smooth platinum electrode was preliminarily subjected to many activations in the range of φ_r from 0.05 to 1.5 V in the investigated solution with the help of potentiostatic sweeps with a rate of 18 mV/sec. The measured potentiostatic curves after this are shown in Fig. 4. On the anodic curve, there are observed three maxima which, according to the data of Will [30], correspond to the ionization of hydrogen adsorbed on various crystal planes of platinum. These three maxima are observed also on the potentiostatic curves of a platinized electrode. In the double layer region of φ_r, no maxima in the current are observed. This agrees with the results of Breiter [31].

If, after activation, the electrode is held for a long time with φ_r in the double layer region (400 mV), and afterwards the potential of the electrode is displaced to 50 mV and the anodic curve is measured, then it practically coincides with the curve 1 of Fig. 4a. However, if after activation, the electrode is held for a long time at potentials in the hydrogen region, then the first potentiostatic curve measured after this has a strong dependence on the purity of the investigated solution and the time of holding. On these curves, at φ_r of approximately 600 mV there is observed a sharply expressed maximum and a third maximum corresponding to strongly bonded hydrogen is markedly depressed. The indicated distortion of the curves is easily observed in the case of solutions prepared from normal bidistillate and various preparations of sulfuric acid (grade V-5 and doubly distilled in vacuum, which are approximately the same).

When particularly pure water is used [23],† subjected to additional adsorption purification on activated charcoal and freshly distilled sulfuric acid is also used, the maximum is strongly decreased. The additional purification of the investigated solution on a large platinized grid, held at potentials in the hydrogen region,‡ enables a still greater degree of purification of the solution so that, after 0.5 h holding of the working electrode at $\varphi_r = 60$ mV, only a very small distortion of the curves is observed in the double layer region. During the recording of periodic potentiostatic curves in the latter solution in the region of potentials where some increase in current had been observed earlier, there was even a decrease in the charge current with increase in φ_r.

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* Another reason for obtaining anomalous electrodes may be the presence of specifically adsorbed cations in solutions used for electrodeposition or for measurements. It is well-known, for example, that ions of lead have an effect on the properties of platinized deposits [27], and catalytic nuclei [28] and surface active cations [29] have an effect on the shape of charge curves.

† The authors express their deep gratitude to N. P. Berezina for supplying the water subjected to the adsorption purification. The normal bidistillate from measurements by N. P. Berezina by the adsorption method of T. A. Kryukova [33] contains $1 \cdot 10^{-7} - 5 \cdot 10^{-8}$ g · mole/liter, and the particularly pure water less than $5 \cdot 10^{-9}$ g · mole/liter surface active materials.

‡ There is interest in the fact that the adsorption of oxidizable impurities occurs only at potentials in the hydrogen region whereas the adsorption of several organic substances is a maximum with φ_r in the double layer [20, 34]. It is possible that the adsorption of impurities is connected with their ability to be subjected to reduction. If the adsorbed impurities have an organic nature, then even their complete oxidation to CO_2 in a closed cell will not enable complete avoidance of the appearance of the "central" plateau with prolonged holding of the electrode with φ_r in the hydrogen region. As was shown by Giner [24], the adsorption of CO_2 on platinum saturated with hydrogen gives a product oxidizable at φ_r in the double layer region.

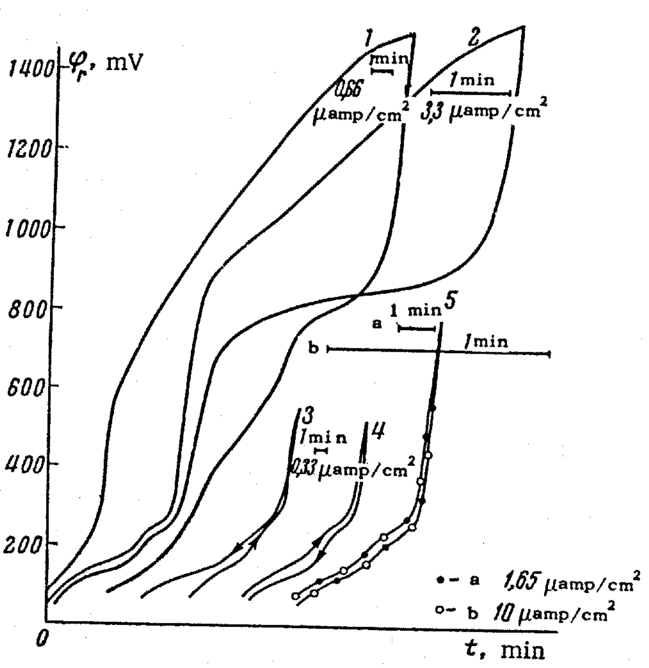

Fig. 5. Charge curves on smooth platinum in 1 N H_2SO_4 at 20°C: 1) complete curve in unpurified solution; 2) the same in purified solution; 3) slow charge curve after activation by method in [39]; 4) the same after activation for 30 min anodically and 30 min cathodically at 100 m amp/cm²; 5) rapid charge curves [1.65 μamp/cm² (a) and 10 μamp/cm² (b)] in a solution subjected to additional purification.

Measurements on very active freshly prepared dispersed catalysts, in spite of careful measures to prevent contamination in the solution, on the other hand, still show a decrease in gradient of the charge curve at $\varphi_r > 550$ mV, not however developing into a plateau. During ageing of the electrode, this phenomenon practically disappears. It is possible that the retardation on the charge curve of dispersed catalyst is connected with the adsorption of oxygen at $\varphi_r > 550$ mV. The results given above on hydrogen adsorption isotherms indicate the presence in the dispersed catalyst of centers with a very high bond energy. The potentials for oxidation of other platinum metals (except palladium, which in relation to oxidation is similar to platinum) is in this region [35-38]. However, the small size of the effect does not enable us to explain its nature by the method of charge curve.

The influence of oxidizable inpurities may also be detected during measurements of charge curves on smooth platinum (Fig. 5). In the case of insufficiently pure solutions and slow recording of the curves, the gradual transition from the double layer to the oxygen region is observed relatively early (at about 550 mV). This may lead us to the conclusion that smooth platinum gives rise to earlier oxidation in comparison with platinized platinum. The regions of adsorption and reduction of oxygen (Fig. 5) are also distorted. With purification of the solution, the arrest point appears in the region φ_r of about 600 mV and after this there occurs complete disappearance of these phenomena. Thus, during measurements of slow charge curves, it is necessary to consider the possibility of contamination of the surface, if special measures for purification of the solution are not taken.

In addition to this, during measurements of slow charge curves ($i < 0.33$ μamp/cm²) there arise on smooth platinum several difficulties caused by the methods of activation of the electrode. Thus, if the electrode, before measurements, was subjected to strong anodic polarization or heating in air, then this leads to dissolution of oxygen [19] in platinum, which during measurements of slow charge curves evolves with a considerable rate on the surface of the electrode and distorts the shape of the curves. We carried out activation of the electrode by the method given earlier [39], which consists of the following: before the experiment, the electrode is polarized for 10 min cathodically (15 m amp/cm²) and 10 min anodically (8 m amp/cm²); after this, the electrode, already in the working solution, is subjected to alternating polarization with 1.8 V and −0.2 V 12 times with a cycle time of 15 sec. After this, charge curves are obtained, the cathodic path of which are much longer than the anodic (Fig. 5, curve 3). This phenomenon may not be explained by traces of oxygen in the solution. The electrode was held, before recording the curves at a potential of about 500 mV, whilst the displacement of φ_r in the anodic direction was only several tenths of a millivolt per minute. The obtained result indicates that considerable quantities of dissolved oxygen are evolved from the surface of the electrode.

The evolution on the surface and the ionization of oxygen distort the curve, beginning at definite potentials, depending on the quantity of dissolved oxygen. When the electrode is held at potentials for hydrogen adsorption, the potential at which the intersection of the curves occurs is displaced in the cathodic direction. This process may be accelerated by strong cathodic polarization. If, after measuring the curves 3 (Fig. 5), the electrode is polarized in a separate vessel cathodically with a current of 100 m amp/cm^2 for 30 min, then afterwards the curves 4 are obtained and the intersection of the anodic and the cathodic curve is absent. The roughness factor of the electrode subjected to such an activation is about 1.4-1.5.

Thus, the construction of the hydrogen adsorption isotherm on smooth platinum may be insufficiently accurate because of the influence of dissolved gases which enter the metal in the preceding treatment. Because the slow charge curves are measured with φ_r of about 80 mV (to avoid the influence of dissolved hydrogen), the extrapolation of the charge curve to zero also must lead to considerable errors in the shape of the isotherm. For these reasons,* in the present work, during the construction of the hydrogen adsorption isotherms on smooth platinum, reference was given to the comparatively rapid measurements (time for recording the curve in the range of φ_r from 50 to 1500 mV was 1.5-7.5 min). As follows from the coincidence of the hydrogen parts of the charge curves measured by various current densities† (Fig. 5), the rate of measurement of the curves was sufficiently small for adsorption equilibrium to be established successfully during the recording of the curves.

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* In the cell used by us for the measurements, in spite of the division of the working parts from the reference electrode with the help of a tap during the galvanostatic experiments, slow diffusion of hydrogen to the electrode from the space for the hydrogen electrode was observed.

† According to the data of Ershler [13], there is a marked dependence of the length of the charge curves on current density. From the presented results, it follows that, in our experiments, a similar effect was not observed.

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