STUDY OF HYDROGEN AND OXYGEN ADSORPTION ON PLATINIZED PLATINUM AT DIFFERENT TEMPERATURES BY ELECTROCHEMICAL METHODS

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According to charge curves and potentiostatic curves for a Pt/Pt electrode in 1 N H_2SO_4, HCl and KOH, when the temperature is raised between 0 and 95° C an increase of about 15-20% is observed in the amount of adsorbed hydrogen. This effect is explained by hydrogen adsorption in poorly accessible regions of the surface at elevated temperatures. Making certain assumptions, we calculated the differential adsorption heats for hydrogen as a function of the coating and compared them with published data. As the temperature increases, it becomes easier for the platinum surface to oxidize and the adsorbed oxygen bond is strengthened. We show the dependence of the reduction in size of the Pt/Pt electrode surface when heated on the potential and composition of the electrolyte solution.

Hydrogen adsorption on a smooth platinum electrode at different temperatures has been studied electrochemically by Breiter and co-workers [1-8]. The measurements they made enabled them to calculate thermodynamic functions describing the behavior of the adsorbed hydrogen. Quantitative studies of the same kind for platinized platinum have not been made. Measurements of the charge curves showed [9] the considerable reduction in size of the platinized platinum surface when heated in electrolyte solutions. According to Sokol'skii and coworkers [10-12], when the temperature is raised the energy of the bond between the hydrogen and platinized platinum surface decreases, while the amount of it $Q_H{}^0$ is appreciably increased. When measuring with low current densities, according to data in [11, 12] $Q_H{}^0$ is approximately doubled when t ranges between 20 and 80°. The increase in the amount of adsorbed hydrogen with temperature on smooth platinum was not noted in [1].

We considered it would be worthwhile to make a detailed study of hydrogen adsorption on platinized platinum at elevated temperatures. Study of the adsorption properties of platinized platinum under these conditions is in addition of considerable interest in connection with the development of research on the kinetics of electro-oxidation of hydrocarbons, which only occurs at appreciable rates when the temperature is raised [13-16].

Procedure for Measurement

In the research we used the charge-curve method and the slow potentiostatic sweep method. The measurements were made in a cell with its working area and comparison electrode immersed in the thermostat. The temperature was controlled with an accuracy of + 0.1° C. When measuring the charge curves the visible surface of the electrode was 30 cm^2, and the volume of the solution in the working area ~ 15 cm^3. The electrode was platinized in a 2% solution of H_2PtCl_6 at a current density of 2 mA/cm^2 for 3 h.

Prior to the experiment, the solution was saturated with hydrogen at the given temperature, after which the electrode potential was shifted by the organ current up to + 60 mV*. Particular attention was given to removing

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* The potentials φ_r are given with respect to the reversible hydrogen electrode in the same solution and at the same temperature as the electrode studied.

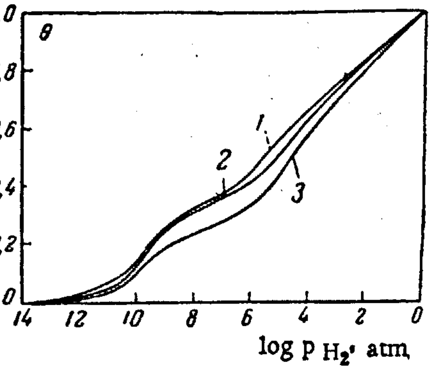

Fig. 1. Isotherms for hydrogen adsorption on a Pt/Pt electrode in 1 N H_2SO_4 at 20° C. 1) Freshly platinized electrode; 2) electrode aged at 0 mV; 3) electrode greatly aged at 500 mV.

hydrogen from the gas phase above the solution in the cell, since the diffusion of hydrogen from the gas phase may introduce initial errors when measuring slow charge curves at high temperatures conducive to diffusion and convection in the solution.

It was found that the relationship between the solution volume, gas phase above it and electrode surface was of great importance for measurements at high temperatures. For example, given a visible electrode surface of 2 cm^2, a solution volume of 15 cm^3 and approximately the same volume of gas phase above the electrolyte, we get unduly high results for the increase in the amount of adsorbed hydrogen with temperature, the reversibility of the charge curves is impaired, and requirements with regard to the purity of the electrolyte have to be stricter.

A number of control experiments were carried out in a special cell with a working area free from the gas phase, with a volume of solution of only 0.05 cm^3 per cm^2 of visible surface. These experiments confirmed the data obtained with the cell described above. Simultaneous experiments were carried out in which we measured the charge curves with displacement of the dissolved hydrogen by inert gas. At the beginning of the charge curve, at 20° C, we observed a gently sloping section associated with ionization of the dissolved hydrogen, although beginning at ~ 30-40 mV the curve proceeds in similar fashion to those obtained after removal of the hydrogen. On the cathodic section of the curve and during secondary recording of the anodic charge curve no such section is observed.

To prepare the solution use was made of doubly distilled water, sulfuric and hydrochloric acids and high-purity KOH. In some of the experiments we prepurified the electrolytes with large platinized grids although this did not make any great difference to the results.

Experimental Results and Discussion

At elevated temperatures we observe a strong reduction of the platinized platinum surface with time [9], which hampers a quantitative study of hydrogen adsorption. Hence, we first conducted experiments to study the aging of the electrode in electrolyte solutions and the concomitant effects. The experiments were carried in 1 N H_2SO_4. The freshly platinized electrode was soaked at 95° C and at varifiable potentials of zero, 500 mV or the potentials at which oxygen is generated. After every two hours of heating the system was cooled down to 20° C, the charge curves were measured and the surface reduction of the electrode was deduced from the length of the hydrogen lag [*]. The results obtained showed that the electrode was aged to the greatest extent when its potential was sustained in the "double layer" region. The aging effects are somewhat less at a zero potential. For example, in the first case, the hydrogen lag on the charge curve dropped by 47% after 4 h, and 36% in the second case. Although the difference in the aging is slight, heating the electrode at different potentials affects the hydrogen adsorption isotherm in different ways. Figure 1 compares these isotherms calculated from the charge curves at 20° C for a freshly platinized electrode and electrodes aged at 0 and 500 mV. The isotherm for the freshly platinized electrode is close to that of a smooth platinum electrode [1]. After the electrode has been heated at a zero potential, the isotherm varies only slightly, whereas the surface reduction at 500 mV is to a marked degree due to loci with a high adsorption potential.

Measurements show that the rapid reduction of the electrode's surface after the first two hours heating then slows down. After a three or fourfold reluction the aging effect in 1 N H_2SO_4 is comparatively weak [†].

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[*] After heating the electrode, there is also a marked decrease in the double layer capacitance, but the reduction in this capacitance is more clearly marked than the reduction in the hydrogen lag, and does not vary in proportion to the latter. Calculation of the electrode surface from the slope of the double layer section of the charge curve involves a number of difficulties, as indicated in [20].

[†] Hydrogen adsorption on the freshly platinized electrode at $\varphi_r = 0$ amounted to ~ 200-250 μ coul/cm^2 of visible surface.

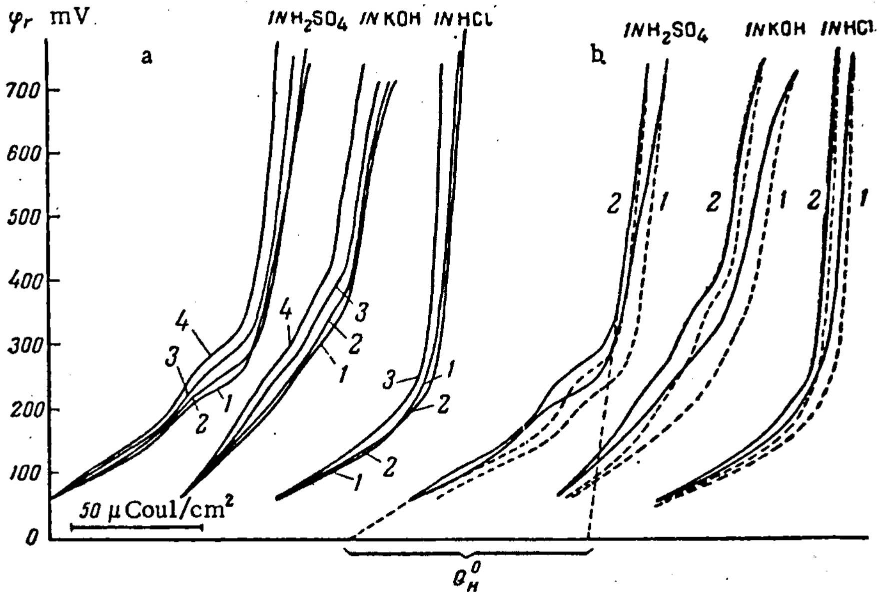

Fig. 2. a) Charge curves for a Pt/Pt electrode at temperatures: 95 (1), 60 (2), 25 (3), 0° C (4) in 1 N H_2SO_4, 1 N KOH and 1 N HCl; i = 100 mA/cm^2; b) anodic and cathodic paths (broken line) of charge curves for a Pt/Pt electrode at 95° C (1) and 20° C (2) in 1 N H_2SO_4, 1 N KOH and 1 N HCl; i = 100 mA/cm^2.

Heating the Pt/Pt electrode at 95° C in a sulfuric acid solution at the oxygen generation potential does not cause a reduction in the surface of the electrode, but results in a slight prolongation of the hydrogen lag with the amount of firmly bonded hydrogen increasing quantitatively. Thus, the oxide layer formed under certain conditions not only stabilizes the platinum surface [17], but may also lead during subsequent deoxidation to slight activation of it. Boiling the electrode in doubly-distilled water to which air has access for 2 h results in a surface reduction by ~ 10 %. This means that the oxide layer forming under these conditions does not yet have adequately protective properties.

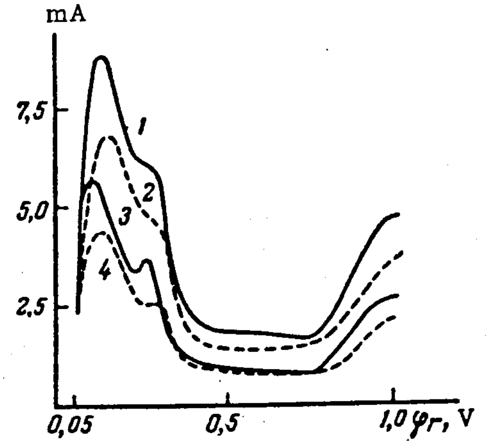

Fig. 3. Potentiometric curves for a Pt/Pt electrode (visible surface 0.1 cm^2) in 0.1N H_2SO_4 at 80° (1,3) and 20°C (2,4) for a scanning rate of 500 (1,2) and 200 mV/sec (3,4).

Aging of the electrode depends not only on the potential, but also on the electrolyte composition. We observed a particularly intensive reduction in surface in hydrochloric acid solutions. The surface of an electrode strongly preaged in 1 N H_2SO_4 is cut down by a factor of about 1.5-2 in a 1 N HCl solution at 500 mV for 2 h at 95°C, and continues to be appreciably reduced as heating continues.

The data we obtained on aging for an electrode heated in an electrolyte solution are to some extent similar to data on the sintering of platinized platinum in a gas phase. For example, in [17] slow sintering of the electrode was observed in an air atmosphere, and more rapid sintering in a hydrogen atmosphere. Yet, according to Shlygin and Nikolaeva* [18], the sintering effect in nitrogen hardly differs from sintering in the presence of oxygen, whereas in the electrolyte solution heating in an inert gas atmosphere at the double layer region potential, as shown above, exerts the greatest effect on the reduction in electrode surface.

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*Data on the sintering of platinized platinum in a gas phase obtained by different authors sometimes fail to tally (see, for example, [18] and [19]).

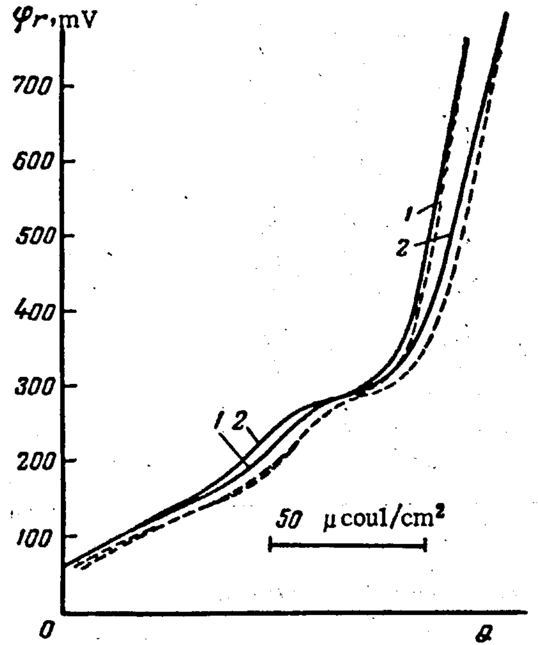

Fig. 4. Charge curves for Pt/Pt electrode in 1 N H_2SO_4 at 20° C after deposition of hydrogen at 20° C (1) and 95° C (2) (cathode path shown by broken line); i = 100 μ A/cm^2.

From then on, we used for measurement of the charge curves and potentiostatic curves for the platinized platinum electrode at different temperatures electrodes that had been preaged by heating at 95° C and a potential of 500 mV.

Figure 2a shows anodic charge curves for a Pt/Pt electrode in 1 N H_2SO_4, HCl, and KOH at different temperatures*. The hysteresis between the anodic and cathodic sections of the curves for different temperatures is small and only slightly increases when the temperatures are raised† (Fig. 2b). Measurement of charge curves using different current densities from 25 to 200 μ A/cm^2) provides results that match; this also shows the good reversibility of the removal and deposition of hydrogen within studied temperature range.

In all the electrolytes used we observe a slight elongation of the charge curve as the temperature rises, as can be seen from Fig. 2. The effect is slightly increased if when comparing the curves we introduce a correction for partial water vapor pressure at elevated temperatures [1]. The latter fact is important for temperatures of 95, 80 and 60° C. The correction $\Delta\varphi$ was introduced by the equation

$$\Delta\varphi = -(RT/nF)\ln(P - P_{el}),$$

where P is the atmospheric pressure, P_{el} is the pressure of electrolyte vapor. In electrolyte solutions the partial pressure was equated by us, as in [1], to the water vapor pressure.

So as to determine the amount of absorbed hydrogen on platinum at different temperatures, we utilized the assumption that total coverage of the electrode by hydrogen is attained at a partial hydrogen pressure of 1 atm, and that the double layer capacitance is approximately constant in the hydrogen region [20]. The correction for double-layer capacitance is shown in Fig. 2b. It should be pointed out that allowance for this correction in sulfuric acid and alkaline‡ solutions leads to greater errors than in hydrochloric acid solutions, particularly at elevated temperatures. This is because of earlier oxidation of the platinum surface with rise in temperature. Furthermore, the lag in the charge curve observed in sulfuric acid solutions at double layer region potentials close to 560 mV at 20° C shifts when the pressure rises toward more cathodic potentials [10]. At 95° C it is already observable at ~ 400 mV. As the electrode ages, the lag is reduced, and it is only slightly marked or even totally absent on greatly aged electrodes. This result is interesting in view of the fact that, as pointed out above, when an electrode is aged in H_2SO_4 the number of loci with an adsorption potential is reduced.

In some papers [11, 22], it was assumed that the lag on the charge curve in H_2SO_4 at double layer region potentials was due to ionization of the dissolved hydrogen. This supposition is unlikely, particularly in view of the data on the influence of electrode aging on this lag. According to Obrucheva [23], the emergences onto the surface of dissolved hydrogen in sulfuric acid solutions requires a long lapse of time.

Calculation shows that elongation of the hydrogen section of the charge curve over temperatures ranging from 0 to 95° C is ~15-20%, i. e., considerably less than pointed out in the literature [11, 12]. This small increase

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*The measurements were made at 0, 20, 25, 40, 60, 80 and 95°C. The diagrams only show curves for 0, 25, 60 and 95° C. The curves for the temperatures inbetween lie between them.

†The paper by Sokol'skii and Kombarov [12] did not devote enough attention to the reversibility of charge curves. According to data given in [10], hysteresis between the forward and reverse path of the charge curves is too great.

‡In an alkaline solution, given this correction, it turns out that the amount of adsorbed hydrogen is ~15% less than in an acid solution for an electrode of the same activity.

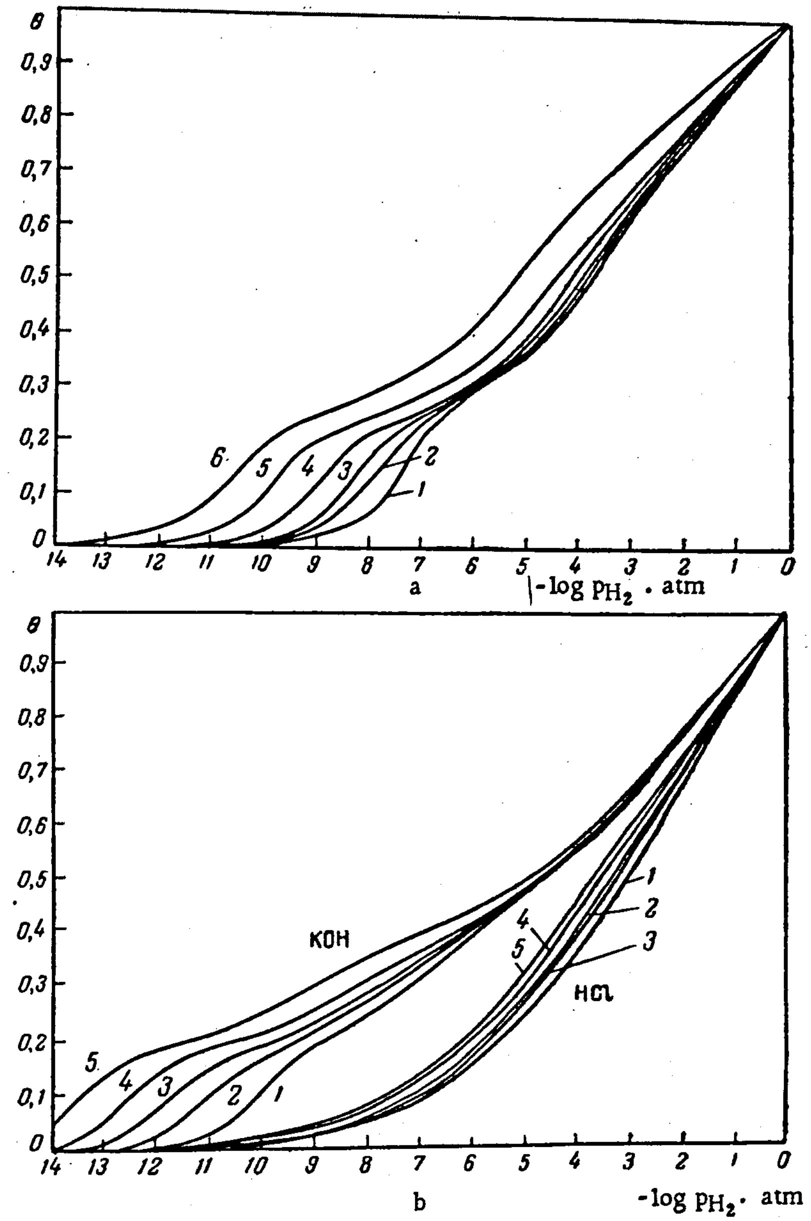

Fig. 5. Isotherms for the adsorption of hydrogen on a Pt/Pt electrode in 1 N H_2SO_4 (a), 1N KOH and 1N HCl (b) at temperatures: 1) 95; 2) 80, 3) 60, 4) 40, 5) 20, 6) 0° C.

in the amount of hydrogen on platinum as the temperature rises is also detected from potentiostatic curves for a platinized platinum electrode in 0.1 N H_2SO_4 (Fig. 3)*.

In our way of thinking, when explaining the increased hydrogen lag on the Pt/Pt electrode as the temperature rises, there is no reason to assume dissolution of the hydrogen in the platinum or activated adsorption of the hydrogen [11, 12]. One of the possible causes of this effect may be hydrogen adsorption at high temperatures on sections of the electrode surface that are inaccessible to adsorption at low temperatures for different reasons (cracks, narrow pores, etc.). This hypothesis is tantamount to the belief that there is a slight increase in the true electrode surface as the temperature rises. The absence of this effect on smooth platinum [1] is evidently associated with the comparatively low degree of roughness.

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*As can be seen from the graph, at the sweep rates used the adsorbed hydrogen is removed in nonequilibrium conditions, which shows up in a change of shape of the potentiostatic curves.

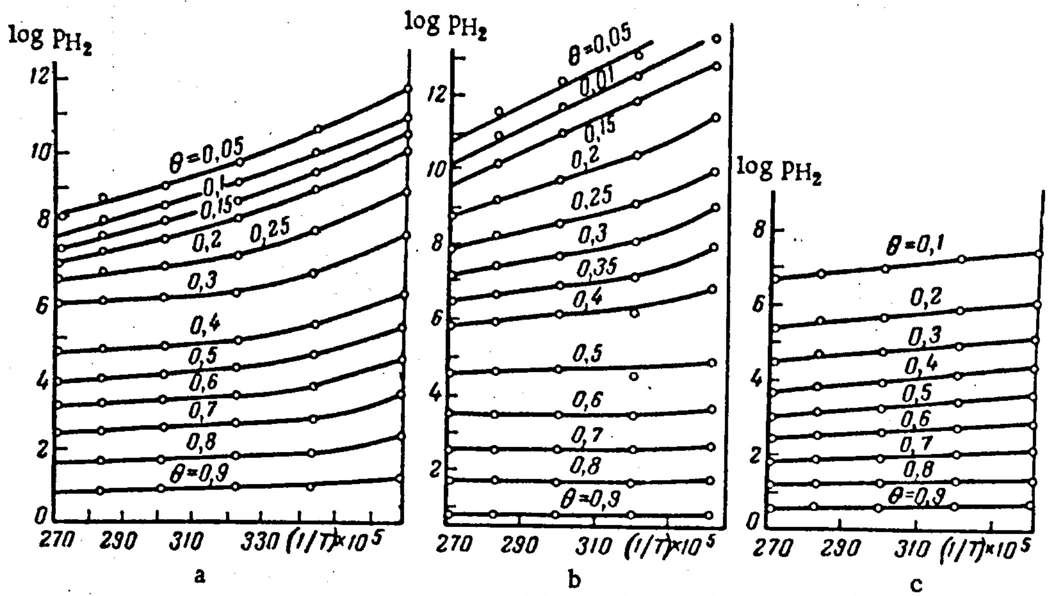

Fig. 6. Isosteres for the adsorption of hydrogen on a Pt/Pt electrode in solutions 1N H_2SO_4 (a) 1N KOH (b) and 1N HCl (c).

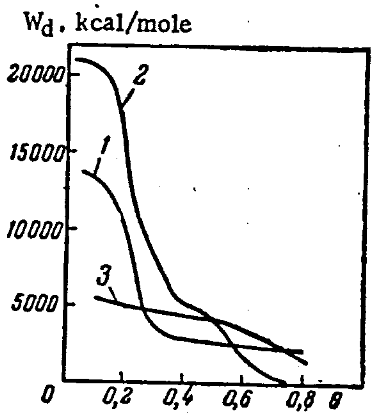

Fig. 7. Differential adsorption heat for hydrogen on a Pt/Pt electrode as a function of degree of coverage in different electrolytes: 1) 1N H_2SO_4, 2) 1N KOH, 3) 1N HCl.

An additional amount of hydrogen adsorbed at high temperatures in H_2SO_4 solutions is not desorbed completely when the solution cools and may be detected in the following experiments. The platinum electrode was saturated with hydrogen at 95° C, after which the temperature was reduced to 20° C and the charge curve measured (Fig. 4). It differs from the curve obtained when all the operations are conducted at 20° C. The curve is longer, with a more gently sloping path in the double layer area, the hydrogen lag is slightly different in shape and hysteresis between the forward and reverse paths of the curve is longer than normal. The subsequent charge curves gradually approach curve 1 in Fig. 4.*

In 1N HCl there effects are much harder observed because of aging rate electrode and possibly spherical adsorption of Cl^-. But even in a case of HCl hysteresis curves measured at 20° C after hydrogen saturation the electrode at 95° C is greater than usual.

Isotherms for hydrogen adsorption at different temperatures on platinized platinum are shown in Fig. 5 and are calculated from the charge curves under the given assumptions. The data were used to obtain adsorption isosteres (Fig. 6), which proved linear in HCl solutions throughout the temperature range, and in H_2SO_4 and KOH solutions between 40 and 95° C. From the slope of the linear segments of the isosteres we determined the differential hydrogen adsorption heats (W_d):

$$(\partial \ln P_{H_2} / \partial T)_\theta = -W_d / (RT^2).$$

Figure 7 shows W_d as a function of the coverage of the surface θ. In all the electrolytes studied there is a reduction in W_d with θ, but the nature of the dependence is complex and we observe a marked deviation from linearity even

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*We considered the possibility of contaminating the Pt/Pt electrode surface with products from the reduction of sulfuric acid with hydrogen at a high temperature. Reduction of H_2SO_4 into hydrogen sulfide by adsorbed hydrogen is definitely observed if the sulfuric acid concentration is 30%. But in 1 N H_2SO_4 this does not seem to occur to a marked extent as it would otherwise lead to considerable deterioration in the reversibility of the charge curves at high temperature.

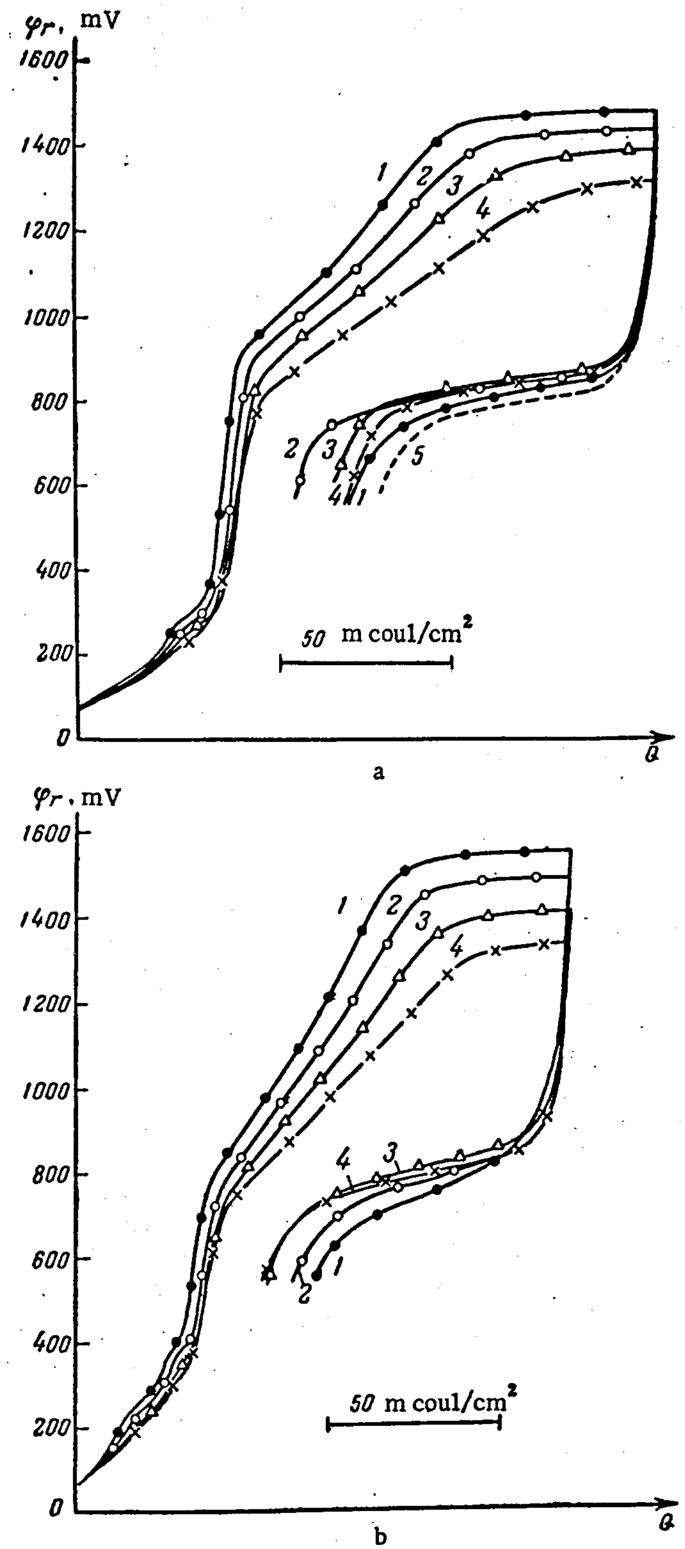

Fig. 8. Charge curves for a Pt/Pt electrode in 1N H_2SO_4 (a) and 1N KOH (b) at different temperatures: 1) 0; 2) 25; 3) 60, and 4) 95° C. Curve 5 was plotted at 25° C after adsorption of the oxygen at 95° C; i = 100 μ a/im^2.

in HCl solutions in which [20] the Temkin isotherm for hydrogen adsorption is manifested best. The curve W_d vs. θ in 1N H_2SO_4 is similar in shape to an analogous curve obtained by Breiter [1, 5] for smooth platinum, although deviations from linearity, according to our data, are slightly more marked, W_d is lower, and high W_d are observed over a smaller range of θ than in [1, 5]. These effects are evidently due to the fact that in our experiments we used aged platinized electrodes with a hydrogen adsorption isotherm different from the isotherms for a smooth platinum electrode, as pointed out above.

The most substantial deviation from Breiter's data is observed at high degrees of coverage. In [1] it was demonstrated that W_d decreases for practically all θ in the series KOH > H_2SO_4 > HCl. According to our own experiments, over a certain coverage range $0.6 < \theta < 0.7$ we observe a different decreasing order in W_d, i. e., HCl > H_2SO_4 > KOH, with W_d dropping to very small values in KOH solutions.

The reasons for this are the same as for the discrepancy with Breiter's data and at the present time are unclear.

The most important point in assessing the amount of hydrogen adsorbed on the platinum surface at different temperatures and in quantiative calculations is the assumption of total coverage of the surface by the hydrogen at a zero potential, although this assumption has been made many times in the literature. In particular, there are indications [21] that on a Pt/Pt electrode total coverage is only attained at room temperature at −50 mV. No verification of this proposition at different temperatures and different electrolyte solutions has been made.

We made an attempt to calculate the adsorption isosteres in an HCl solution by another method. It was first assumed that at double layer region potentials in 1 N HCl coverage by adsorbed hydrogen was nil. Then, beginning at $\theta_H = 0$, we found potentials and partial hydrogen pressures corresponding to identical quantities of H_{ads} at different temperatures. This method, however, did not produce satisfactory results: the adsorption isosteres prove nonlinear and at large θ the slope of them reverses direction, corresponding to negative W_d. This is evidently due to the increased amount of adsorbed hydrogen on the electrode when the temperature rises.

Measurement of complete charge curves (up to the hydrogen generation potential) show the great effect of temperature on oxygen adsorption on a platinized platinum surface (Fig. 8). At elevated temperatures oxidation of the platinized platinum is made easier and the oxygen generation commencement potential shifts toward the cathode from ~1550 mV at 0° C to ~1335 mV at 95° C in 1 N KOH, and from ~1475 to ~1315 mV in 1 N H_2SO_4, given a current density of 100 $\mu A/cm^2$. The behavior of the charge curve in the oxygen region at elevated temperatures becomes more linear. Just as in the case of hydrogen adsorption, we observe a ~25% increase in the amount of adsorbed oxygen within the temperature range 0 to 95° C.

There is no such clearly marked regularity in the cathodic shape of the charge curve for the oxide layer reduction potentials as there is for the potential at which the electrode oxidizes and oxygen is generated, particularly in a sulfuric acid solution. At higher temperatures the oxides are in certain cases reduced at a more cathodic potential than at lower temperatures. This effect seems to be due to competition between the two effects: acceleration of the oxide reduction process at high temperature and stronger bonding between the oxygen and the surface under these conditions. Indeed, if we oxidize the surface of an electrode by anodic polarization at 95° C and measure the cathode charge curve at 25° C, we observe a shift in the lag on the charge curve toward the cathode (Fig. 8a, curves 4 and 5). Measurement of the charge curves also shows that the bond between the oxides formed at 25° C and the electrode surface strengthens as the temperature rises.

We are indebted to Academician A. M. Frumkin for suggesting this topic and for his constant interest and advice.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
