HYDROGEN ADSORPTION ON PLATINUM METALS AT DIFFERENT TEMPERATURES

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The authors have measured and analyzed the charging curves on rhodiumized and ruthenized electrodes and on skeletal osmium and iridium in the range 20-95°C in 1 N H_2SO_4 and 1 N NaOH.

In our previous reports [1, 2] we studied how hydrogen adsorption on different specimens of a platinum catalyst varies with temperature by the charging-curve method. The present work deals with similar measurements on the other platinum metals with developed surfaces, with the exception of palladium, for which the literature gives sufficient information [3].

Hydrogen adsorption on iridium, rhodium, osmium, and ruthenium was studied in [4-15]. By means of the potentiostatic method, Breiter et al [6, 7] obtained the first quantitative data on the variation of the differential heat of adsorption with the degree of electrode coverage by hydrogen on smooth iridium and rhodium. The adsorption isotherm of hydrogen on a rhodiumized electrode was analyzed by Tyurin [10]. The authors of [12] and [13] obtained data on the effect of temperature on the charging curves of rhodiumized and ruthenized electrodes. However, these results are only qualitative and, in the case of a rhodiumized electrode, heating at higher temperatures led to distortion of the charging curve in the double-layer region.

Method of Measurement and Preparation of the Electrodes

In this work we used the charging-curve method. The design of the electrolytic cell and the measurement procedure are described in detail in [1]. We used catalysts electrodeposited on a platinum grid (with visible surface 30 cm²) and skeletal catalysts.

A ruthenized electrode was made by the method in [14] from 0.1 N KOH with simultaneous solution of the anode with ruthenium powder. A rhodium electrode was made by electrodeposition from a rhodium chloride solution at current density 6 mA/cm² of visible surface.

We made skeletal catalysts from osmium, iridium, and rhodium. For this purpose 40 at.% of the powdered metal was mixed with 60 at.% of aluminum powder, and tablets were pressed from the mixture; these were sintered for 30 min in a quartz tube in hydrogen at ~750°. The sintered product was enclosed in fine platinum gauze and treated with a concentrated alkali solution and then, at the control potential, in 1 N H_2SO_4 at 95°, i.e., at the highest experimental temperature. Ir–Al and Rh–Al alloys were treated at the oxygen evolution potential, the Os–Al alloy at potential 600 mV to avoid anodic solution of osmium.

In the case of skeletal catalysts, even prolonged treatment did not remove all traces of Al, particularly in the case of Ir–Al alloy, which was the most compact of those obtained. As a result, we observed considerable prolongation of the oxygen sector of the electrodes' charging curves, particularly at higher temperatures, evidently owing to anodic solution of aluminum at the oxygen deposition potentials. In the case of Ir–Al alloy, the distorting effect of aluminum on the oxygen sector was observed at 95°C, even after prolonged anodic polarization of the electrode at this temperature. For quantitative calculations we therefore used the adsorption isotherms for the range 20-80°.

At zero potential, the hydrogen adsorption capacities of the freshly prepared electrodes were as follows: Rh (electrolytic) 0.32 coul/cm², Rh (skeletal) 73 coul/g, Ir (skeletal) 52 coul/g, and Os (skeletal) 80 coul/g. Heating to 95° was accompanied by a slight reduction (~10-15%) of the electrode surface in the case of Os, Ir, and Ru, but a considerable reduction (~45%) in the case of Rh. The experiments were performed after the electrode surface had been stabilized by prolonged heating at 95°C.

The φ_r potentials were measured relative to a reversible hydrogen electrode in the same solution at the experimental temperature.

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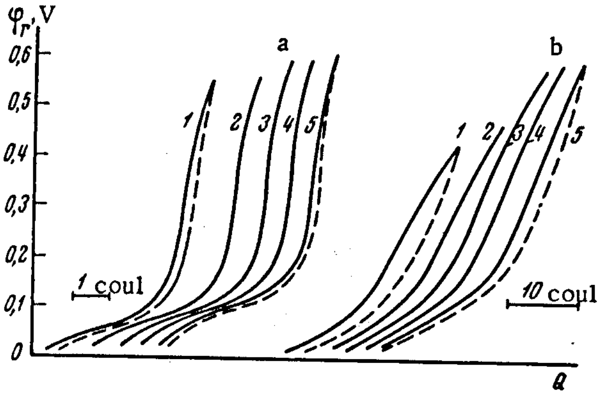

Fig. 1. Charging curves of rhodium (a) and osmium (b) electrodes in 1 N H_2SO_4 at 95° (1), 80° (2), 60° (3), 40° (4) and 20°C (5). i = 200 μA/cm² (a), i = 75 mA/g (b); the dashed lines are the cathode branches of the curves.

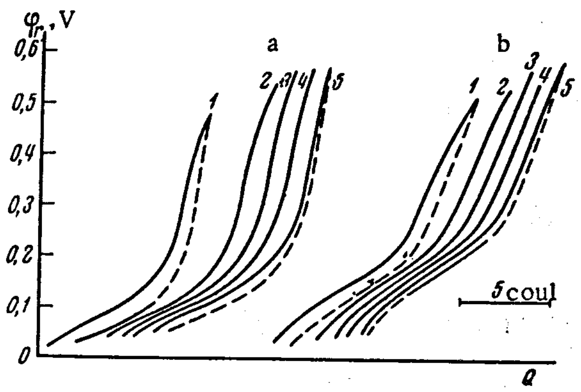

Fig. 2. Charging curves of a skeletal iridium electrode in 1 N H_2SO_4 (a) and 1 N NaOH (b) at 95° (1), 80° (2), 60° (3), 40° (4), and 20°C (5). i = 30 mA/g; the dashed lines are the cathode branches of the curves.

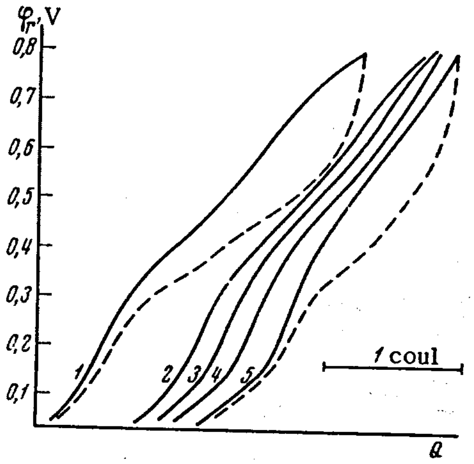

Fig. 3. Charging curves of a ruthenium electrode in 1 N H_2SO_4 at 95° (1), 80° (2), 60° (3), 40° (4), and 20°C (5); i = 100 μA/cm²; the dashed lines are the cathode branches of the curves.

EXPERIMENTAL RESULTS AND DISCUSSION

On all these electrodes we measured the charging curves in 1 N H_2SO_4 at 95, 80, 60, 40, and 20° (Figs. 1-3). According to Obrucheva and Rubinshtein [10], on electrodeposited iridium the strength of the adsorbed hydrogen bond in alkali is less than in acid (unlike the other platinum metals); on skeletal Ir we therefore also measured the charging curves in 1 N NaOH.

On the rhodium and iridium electrodes the amount of adsorbed hydrogen Q_H^0 at $\varphi_r = 0$ is virtually independent of temperature (the differences between the Q_H^0 values at different temperatures are less than the experimental error).* An exact assessment of the effect of temperature on hydrogen adsorption on osmium and ruthenium is impeded by the rapid oxidation of their surfaces and partial screening of the regions of hydrogen and oxygen adsorption (Figs. 1 and 3). Rao et al. [17] attribute this early oxidation of Os and Ru to their electron structures. We must probably also take into account the structural differences between the platinum metals. Whereas all the other platinum metals have cubic structures, ruthenium and osmium have hexagonal lattices, which are possibly more easily penetrable by oxygen atoms.

We cannot assess the ratio of the amounts of adsorbed hydrogen and oxygen on osmium and ruthenium because these metals begin to dissolve even at relatively low anode potentials.

Earlier oxidation of the surface at higher temperatures must be noted as a general characteristic of platinum metals.

On the charging curves of iridium and rhodium in acid solutions the double-layer region is fairly distinct (Figs. 1 and 2) and the regions of oxygen and hydrogen adsorption are sufficiently distinct to enable us to draw quantitative conclusions on hydrogen adsorption. The charging curves display a high order of reversibility. The charging curves on skeletal rhodium coincide exactly with those on a rhodiumized electrode. In the case of iridium, as we go from 1 N H_2SO_4 to 1 N NaOH we observe an approximately threefold increase in capacity in the double-layer region, evidently due to overlapping of the regions of hydrogen and oxygen adsorption. Therefore in the given case a correction for charging of the double layer, and the determination of the hydrogen adsorption region, can only be very approximate; the calculations given below are therefore only rough assessments. In the

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* Khomchenko et al. [12, 13, 16] observed an increase in hydrogen adsorption to a certain value at higher temperatures if the measurements were performed on fresh electrodes with a sequential increase in temperature. We performed similar measurements on a Pt/Pt electrode and observed only a decrease in hydrogen adsorption due to recrystallization of the electrode surface.

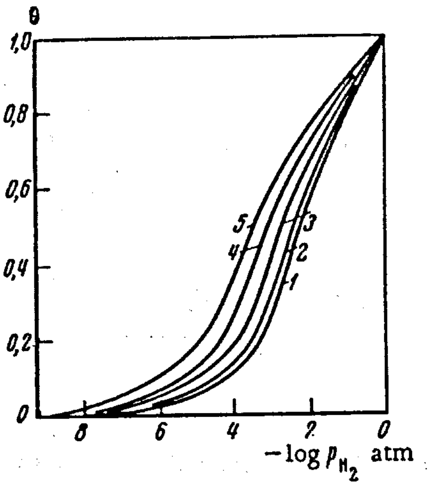

Fig. 4. Isotherms of hydrogen adsorption on a rhodiumized electrode in 1 N H_2SO_4 at 95° (1), 80° (2), 60 (3), 40° (4), and 20°C (5).

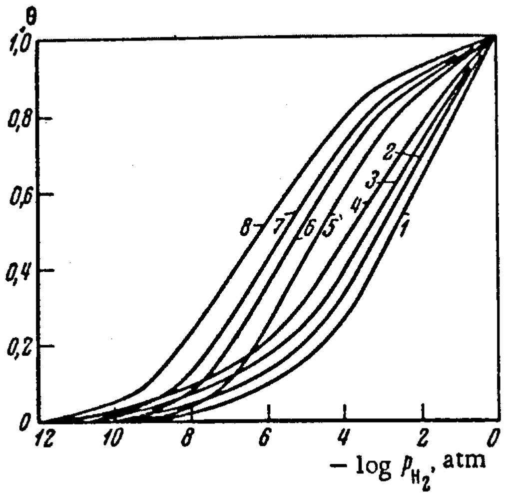

Fig. 5. Isotherms of hydrogen adsorption on a skeletal iridium electrode in 1 N H_2SO_4 (1-4) and 1 N NaOH (5-8) at 80° (1, 5), 60° (2, 6), 40° (3, 7), and 20°C (4, 8).

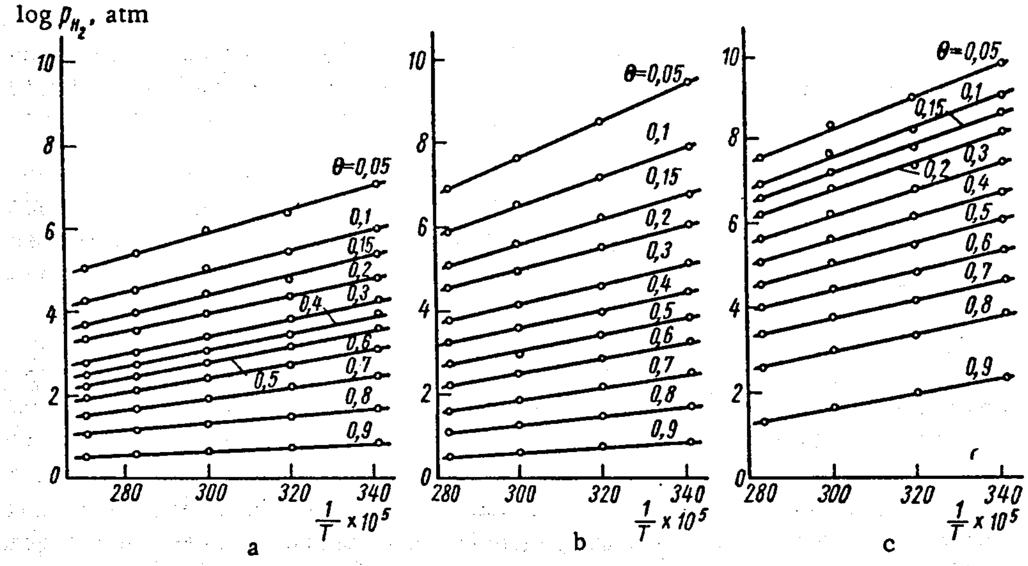

Fig. 6. Isosteres of hydrogen adsorption on rhodium (a) and iridium (b, c) electrodes in 1 N H_2SO_4 (a, b) and 1 N NaOH (c).

case of iridium, in passing from acid to alkali we observe an increase in the bond energy of the adsorbed hydrogen, like that for the other platinum metals.

According to Breiter [6, 7], the potentiostatic curves of smooth iridium have two maxima in the hydrogen region. The charging curves of skeletal iridium do not have two distinct lags corresponding to the two maxima on the potentiostatic curves.

At coverages greater than 0.2, rhodium has a very weak bond with hydrogen, so that most of the adsorbed hydrogen is already removed at very low potentials. For example, at 95° approximately half the adsorbed hydrogen (allowing for the pressure of the electrolyte vapor by a correction to the calculations [6, 7]) is removed before φ_r = 50 mV. Therefore the measurements of the charging curves were performed in relation to temperature with φ_r 10-20 mV.

For iridium and rhodium we calculated the hydrogen adsorption isotherms for different temperatures (Figs. 4 and 5), making the same assumptions as in [1]. Owing to lack of data on the potentials at which total coverage by hydrogen is reached on these metals, we made the arbitrary assumption that total coverage is observed at $\varphi_r = 0$.

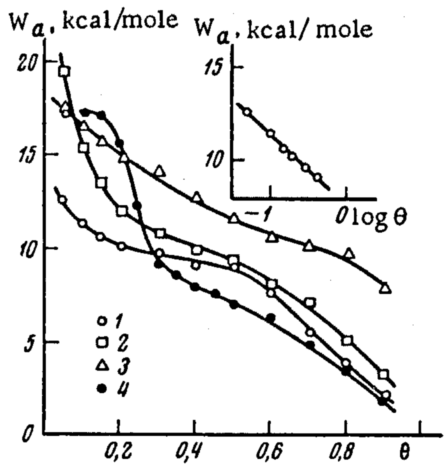

Fig. 7. Differential heat of adsorption of hydrogen versus degree of coverage on different electrodes in 1 N H_2SO_4 (1, 2, 4) and 1 N NaOH (3): 1) rhodium electrode; 2, 3) skeletal iridium; 4) Pt / Pt electrode.

Since the amount of adsorbed hydrogen on these electrodes is independent of temperature, the same coverages correspond to the same quantities of electricity at all temperatures. Therefore the isosteres obtained at different temperatures are comparable and can be used for constructing the adsorption isosteres and calculating other quantitative characteristics of hydrogen adsorption.

On the isotherms of hydrogen adsorption on rhodium, as noted in [10] we distinguish two different regions, described by the Temkin [18] (average coverages) and Freundlich (small coverages) isotherms. Over a large range of coverages the adsorption isotherms on iridium in 1 N H_2SO_4 and 1 N NaOH are described by the Temkin isotherm. In the temperature range investigated the isosteres of hydrogen adsorption on iridium and rhodium are linear (Fig. 6), in contrast to Breiter [6] who indicates that linear relationships are obtained for rhodium only at >50° and for iridium only with $\theta > 0.3$.

Figure 7 plots the diffential heats of adsorption of hydrogen, calculated from the isosteres, versus the degree of coverage. In every case we observe a decrease in the differential heat of adsorption with increasing coverage. On rhodium, at coverage ~0.5 the curve has a break. This corresponds approximately to the coverage range at which the Freundlich isotherm changes over to the Temkin isotherm. At coverage < 0.5 the (W_a, log θ) curve is a straight line, which corresponds to the Freundlich isotherm. On iridium, the differential heats of hydrogen adsorption in alkali are greater than in acid, and, in the range where the Temkin isotherm holds true, the (W_a, θ) curve is approximately linear.

Our results agree qualitatively with those of Breiter for smooth platinum metals.

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