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ON THE PASSIVITY OF PLATINUM

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It has been shown in an earlier communication (¹) that an exponential dependence is observed between the velocity of dissolution of platinum and the amount of oxygen adsorbed on its surface. Such a result compels to suppose that the oxide film on platinum has a retarding influence upon the process of dissolution which cannot possibly be reduced to mere blocking of the surface of the metal. Particular interest attaches therefore to the mechanism of the dissolution process, since it may be expected that the passivation of platinum is caused by the retarding «catalytic effect» of oxygen upon the slowest stage of this process. Having found no data in the literature upon the kinetics of dissolution of platinum, the author attempted to fill the gap by this study. As shown below, the author's results permit to think that in the case of anodic dissolution of platinum in hydrochloric acid we have to deal with an electrochemical mechanism of dissolution; it is understood that this is such a mechanism, according to which the slowest stage is connected with the movement of charged particles across the electric field at the surface of the metal.

I. Experimental. The process might be characterized by the dependence of its velocity upon the potential under the conditions excluding the formation of the passivating oxide film. However, the dissolution of smooth platinum in hydrochloric acid solutions proceeds with discernible velocity at such potentials which permit the formation of oxides. Only at very low densities of the anodic current alone, i. e. at sufficient cathodic potentials, may it be expected that the process of dissolution will proceed upon an unoxidized surface. However, at low densities of the anodic current the results of measurements effected with a smooth electrode are not reliable on account of the depolarizing effect of impurities present in the electrolyte, as a certain part of the current is spent on their oxidation. Therefore, the measurements have been carried out with a platinized electrode having a developed surface and fitted for the application of very low density currents. Such an electrode gives in general more reproducible results.

An electrode in the form of a wire with an apparent surface of 1 cm² was platinized in 2% solution of $PtCl_4$ using a 5 mA current during 30 min., it remained shining after this treatment. Then the electrode was rinsed with distilled water and instantly used for measurements. Its actual surface (as determined from the charging curve) amounted to about 300 cm². The runs were carried out in a solution from which oxygen had been eliminated by bubbling nitrogen through it.

At the beginning the weakest anodic current used in the dissolution tests was passed through the electrode. The potential increased rapidly and afterwards but slowly changed with time. The electrode was exposed to this current for 1 to 2 min., then the current was increased twofold, and we waited once more till a more or less constant potential was established. In this way the current strength was brought up to the values at which the passivation started*. The results of these measurements in the case of 15 N H_2SO_4 with various additions of hydrochloric acid are plotted in Fig. 1. From it it is seen that each time that the strength of the current was doubled, the potential increased by as much as 35—40 mV. We observe here therefore an exponential dependence of the velocity of dissolution upon the potential; the curve representing the relation between the logarithm of the current and the potential shows a slope of 120 to 130 mV**. Thus, it may be approximately assumed that the velocity of dissolution increases with the potential φ according to the law:

$$\text{const}\ \exp\left[\frac{\varphi F}{2RT}\right].$$

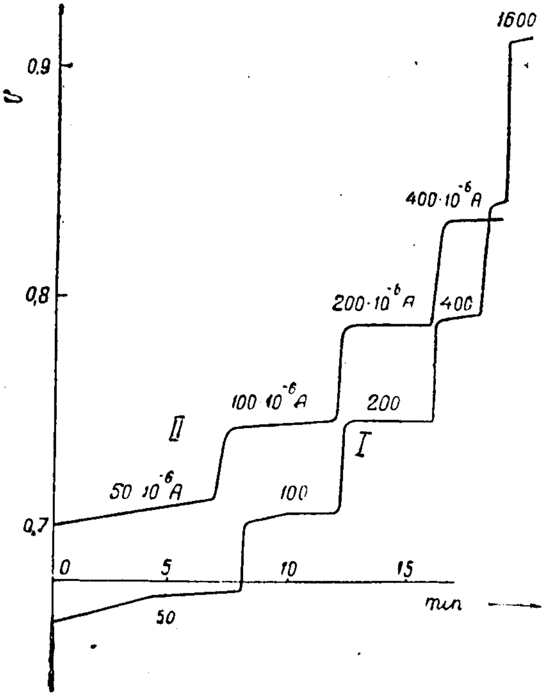

Fig. 1. Dissolution of platinized platinum in concentrated solutions of acids. I—15 $N H_2SO_4$ saturated with HCl; II—15 N H_2SO_4 + 0.18 N HCl.

The potentials were measured against the reversible hydrogen electrode in 5 N H_2SO_4 (a verification of the exponential law is possible only in a limited interval of potentials, since with the increase of the latter passivation eventually takes place).

To a certain degree this result may be interpreted to mean that the slowest stage of the dissolution process is the discharge or the formation of an univalent ion. For instance, it may be supposed following Leblanc, that this stage consists in the discharge of a chlorine ion upon an atom of platinum, whereby the bond between this atom and the lattice of the metal is weakened. If this latter assumption is correct, the velocity of dissolution will be proportional to the surface concentration of chlorine ions. Experi-

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* The latter manifested itself by a considerable increase of the potential observed after the current strength was increased twofold and also by the evolution of the chlorine upon the electrode.

** In computing the angle of slope, the increment of the potential, observed immediately after the strength of the current was doubled, was divided by log 2. It is difficult to draw the «logarithm of current—potential» curve, since the potential does not remain strictly constant at a given current intensity, but rather shows a steady though slow increase, thus making it impossible to choose the value of the potential corresponding to a given current. This slow increase of the potential is probably due to the fact that the surface of the electrode diminishes by dissolution, or, in other words, is caused by the growth of the actual density of the current.

ments on the effect of the concentration of HCl upon the velocity of dissolution have to a certain degree confirmed this conclusion. The runs have been carried out in 15 N H_2SO_4 solutions which contained hydrochloric acid in various concentrations*. In these solutions the curves in Fig. 2, analogous with those in Fig. 1, have been measured. Since foreign anions are here greatly in excess and, besides, the concentration of chlorine ions is low, the surface concentration of the latter will be proportional to their bulk concentration, and therefore the data in Fig. 1 bear witness to the proportionality between the surface concentration of ions and the velocity of dissolution.

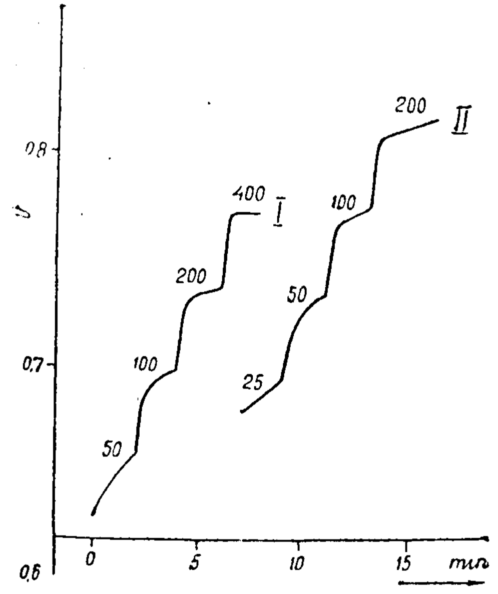

Fig. 2. Dissolution of a platinum electrode in: I — 15 N H_2SO_4 + 0.4 N HCl; II—15 N H_2SO_4 + 0.1 N HCl.

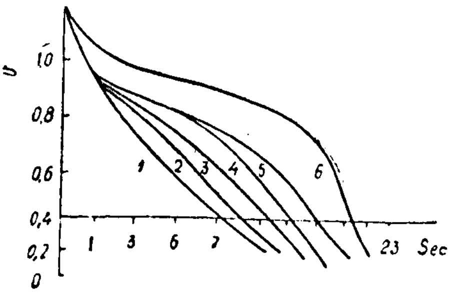

Fig. 3. Cathodic curves for platinum electrode after dissolving it in 0.4 NHCl at 1.14 V at different rates: *1* curve—1 600×10^{-6} A; *2* curve—400×10^{-6}A; *3* curve—100×10^{-6}A; *4* curve—25×10^{-6} A; *5* curve—7×10^{-6} A; *6* curve—0 × 10^{-6} A.

II. Since the data on passivation of platinum, given in the first communication, have been obtained with a smooth electrode and the data on the kinetics of dissolution cited above with a platinized one, the experiments on passivation had to be repeated with the latter. In this case, no experiments with alternating current even of relatively low frequency can be realized on account of the great actual surface of the electrode. Therefore, we have confined ourselves only to experiments on gradual passivation of the electrode at constant potential. For that purpose the platinized electrode was reduced in a HCl solution by cathodic polarization until a potential of +0.1 volt against the reversible hydrogen electrode in the same solution was reached, and then by means of anodic current of large density it was brought to a certain previously selected anodic value of the potential. This final potential was selected in such a way as to provide the realization of both processes, that of dissolution and that of passivation. Instantly after the final potential had been attained, the cathodic polarization curve has been measured by means of an oscillograph (Fig. 3). The length of the horizontal portion observed on such curves at anodic potentials is equivalent to the amount of oxygen adsorbed on the electrode at the time preceding

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* In the first place in a 15 N H_2SO_4 solution, that contained no hydrochloric acid, the charging curves of the platinized electrode have been measured at potentials, at which dissolution of platinum takes place in the presence of HCl. The coincidence of the anodic and cathodic polarization curves in the absence of HCl bore witness to the fact that under these conditions the process of dissolution practically failed to take place.

the measurement of the curves. On curve *1* (Fig. 3) there is nearly no horizontal portion at all because no discernible amount of oxygen had time to be adsorbed upon the electrode during the short interval when it was kept at anodic potentials.

The next experiment was carried out in the same way, but when the final potential was attained, the current was slowly decreased having all the time in mind to keep the value of the potential constant. The strength of the current which is necessary to provide a constant value of the potential in these runs we shall consider equivalent to the velocity of dissolution; in other words, we disregard the portion of the current corresponding to oxidation and assume that all the current is spent upon dissolution.* When the current strength (velocity of dissolution) was decreased 4 times compared to the initial one, the cathodic curve was measured once more (curve *2*, Fig. 3). Then the run was repeated, but the final potential was kept constant till the velocity of dissolution decreased 16 times as compared to the initial one (curve *3*), then 64 times (curve *4*) and, finally, 256 times (curve *5*). By examining Fig. 3 we are convinced that when the velocity of dissolution decreases in geometrical progression, the amount of oxygen on the surface grows according to a linear law, i. e. in the case of a platinized electrode an exponential dependence is observed between the velocity of dissolution and the amount of adsorbed oxygen identical with that previously found with a smooth electrode (1).

It should be mentioned that according to Fig. 3 the velocity of dissolution decreases 4 times when a very small part of the surface is coated with oxygen. The amount of oxygen effecting this decrease of the velocity of dissolution corresponds to the distance between the descending branches of two adjacent curves (Fig. 3). A computation shows that this amount of oxygen atoms may block about 6% of the surface atoms of the metal**.

Conclusions. 1. The assumption has been advanced that the reaction of a chlorine ion with a surface atom of the metal is the slowest stage in the process of dissolution of platinum in hydrochloric acid. The dependence of the velocity of dissolution upon the potential of the electrode and the concentration of chlorine ions, discussed in this study, confirms this assumption.

2. It has been shown that the exponential dependence of the rate of dissolution on the amount of adsorbed oxygen, previously found for the smooth electrode, is observed in the case of a platinized electrode as well.

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REFERENCES

1 Б. Эршлер, ЖФХ, 14, 357 (1940).

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* The correctness of this assumption may easily be verified by comparing the charge introduced by anodic current into the electrode from the moment of attaining the final potential to the moment of measuring the curve, with the charge equivalent to the amount of the oxides formed during the same period as found from the cathodic polarization curve.

** Assuming that when all the surface of the metal is blocked, an atom of oxygen will be adsorbed per each surface atom of platinum.