Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1942. Volume XXXVII, № 7—8

PHYSICAL CHEMISTRY

ELECTROCHEMICAL MECHANISM OF PASSIVATION OF PLATINUM

By B. V. ERSHLER

(Communicated by A. N. Frumkin, Member of the Academy, 7.IX.1942)

The exponential relation between the velocity of dissolution of platinum and the degree of covering of its surface with oxygen demonstrated by various experiments (1) is difficult to explain, if the passivation is looked upon as a process of formation of a protective oxide film, which isolates the metal from the solution. The quantities of oxygen involved are so insignificant that the possibility of simple isolation of the metal from the solution by the oxide layer is quite out of the question. For instance, by covering only 6% of the surface of platinum with oxygen the velocity of dissolution is diminished as much as 4 times, and so an effect is attained which, should it be a mere blocking effect, would not have taken place unless 75% of the surface of the metal had been covered by the protective layer. If the strong retarding effect of small amounts of oxygen can be explained qualitatively on the basis of the blocking action by assuming that only a small part of the surface atoms of the metal are capable of dissolving with noticeable velocity and that it is sufficient to block these atoms in order to retard the dissolution, yet the exponential law, according to which the dissolution rate is decreased with the increase of the degree of covering, admits of no such explanation at all*. The existence of such a law may serve as an indication that in this case oxygen retards dissolution by rising the potential barrier to be surmounted by dissolving atoms. This effect may be similar to the well known retarding action of adsorbed oxygen upon the emission of electrons from incandescent metals which increases according to an exponential law with the degree of covering of the surface. A. Shlygin, A. Frumkin and V. Medvedovsky (2) have recently found the adsorbed oxygen to have a strong effect upon the structure of the electric field at the surface of the platinum electrode; A. Frumkin** believes that the passivating effect may be connected with the displacement of anions from the double layer by oxygen atoms.

Considering the mechanism of passivation from this point of view, the following explanation of the exponential law is possible.

---

* The explanation of the exponential law on the basis of the blocking effect is possible only on the assumption that the distribution of surface atoms of platinum according to the energy of their bonds with the metal obeys a linear law. There is little probability in this conjecture, however, since it is natural to expect that this distribution will follow the Boltzman law (see B. Ershler «The Mechanism of Passivation of Platinum», dissertation, Karpov Institute of Physical Chemistry, 1941).

** Private communication to the author.

Since, according to this author's data, the dissolution of platinum follows the mechanism of retarded discharge, the rate of dissolution must decrease exponentially with the decrease of the potential drop in the double layer. The latter in its turn decreases with the adsorption of oxygen (²), the change being approximately proportional to the amount of adsorbed oxygen*. Thus, when the passivation is carried out at constant potential, the drop of potential in the double layer will fall according to a linear law, when the amount of adsorbed oxygen increases according to the same law, and this in turn will affect the rate of dissolution which will decrease in accordance with an exponential law. On this theory the retardation of dissolution by oxygen is due to the weakening of the electric field of the double layer, which leads to an increase of the energy of activation for the reaction of chlorine ions with platinum**. This mechanism of the passivation by oxygen may properly be described as electrochemical.

The data by Shlygin, Frumkin and Medvedovsky as well as my own measurements allow to compute the retardation of dissolution which should be observed in the course of adsorption of oxygen in the case of the electrochemical mechanism of passivation. In doing so it is convenient to use the ratio of the «capacities» of the ionic and atomic layers, i. e. the ratio between the charges that should be expended in order to form (upon 1 cm^2 of the surface of Pt) an atomic and a ionic layer, respectively, corresponding to a potential drop of 1 volt. This ratio may be estimated as 4.7, as follows from computations based on comparing the results of adsorption measurements on platinum electrode with the charging curves.

Let us now consider the passivation of an electrode at constant potential. The electrochemical equivalent of oxygen, covering 6% of the surface of a smooth platinum electrode with a surface area 1 cm^2, equals 2.5×10^{-5} coulombs***. The electrical equivalent of anions displaced by this oxygen from the double layer will equal $\frac{2.5 \times 10^{-5}}{4.7} = 0.53 \times 10^{-5}$ coulombs; the decrease of the charge of the double layer by 0.53×10^{-5} will lead to a decrease of the drop of potential equal to $\frac{0.53 \times 10^{-5}}{70 \times 10^{-6}} = 0.076$ volt, where 70×10^{-6} farad is the capacity of the double layer on platinum at a positive charge of the surface according to earlier measurements. Taking into consideration the dependence of the velocity of dissolution upon the potential of the double layer in agreement with our measurements (see preceding communication), we shall find that when 6% of the surface is covered with oxygen, the velocity of dissolution should decrease approximately 4 times. This agrees with the results of direct measurements, since in our experiments the velocity actually dropped 4 times under these conditions. The quantitative coincidence in this case is

---

* The layer of dipoles, formed by adsorbed oxygen atoms with the surface atoms of platinum, produces a potential difference having the same sign with that of the double layer, when the surface is positively charged. If, for instance, the passivation is carried out while the potential of the electrode is kept constant, the increase of the potential drop in the atomic layer due to the increasing quantity of adsorbed oxygen is attended by an equal decrease of the drop in the ionic layer, and the sum of the potential differences is not altered. Since the drop of potential in the atomic layer increases proportionally to the quantity of oxygen atoms, composing this layer, the drop of potential in the ionic layer decreases in proportion with the quantity of adsorbed oxygen.

** The drop of potential produced by the atomic layer is supposed to be localized in the interior of the metal and to have no effect therefore upon the electrochemical reaction.

*** It is assumed that the electrical equivalent of oxygen, completely covering the surface area 1 cm^2, equals 0.42×10^{-3} coulombs.

certainly not essential, but the order of magnitude for the effect is obtained correctly. The same result may be obtained in a more simple way. Examination of adsorption curves and of the effect of oxygen upon them (²) brings us to the conclusion that the drop of potential in the atomic layer of oxygen on the surface of platinum in an aqueous solution amounts to 0.5—1 volt; 6% of this value makes 0.03 to 0.06 volt, and this is approximately the change which takes place in the potential drop lying in the ionic double layer when 6% of the surface are covered with oxygen. Accordingly, the rate of dissolution will change 2 or 3 times, i. e. we obtain an effect of the same order of magnitude as before.

It is to be regretted that no sufficient data are available to verify finally this electrochemical theory of the passivating action of oxygen. This theory includes 2 assumptions which need checking:

1. The assumption that the atomic drop of potential is localized in the interior of the metal, made by the author (see footnote on page 231), is equivalent to the assumption that the surface of the metal remains electrically homogeneous after the adsorption of oxygen.

2. The displacement of anions by oxygen atoms from the double layer has been reliably observed in the case of sulphate ions. Here this observation is transferred upon chlorine ions without any verification.

As further study in this direction has been put off for an indefinite time, it seemed meanwhile expedient to make known the results already obtained and to advance their probable interpretation.

Karpov Institute of Physical
Chemistry.

Received
7.IX.1942.

REFERENCES

[1] Б. Эршлер, ЖФХ, 14, 357 (1940); C. R. Acad. Sci. URSS, this issue.
[2] A. Shlygin, A. Frumkin and V. Medvedovsky, Acta physicochimica, 4, 911 (1936).