

The Platinum Electrode

V¹. The measurement of the capacity of a smooth platinum electrode when charged with currents of low density

By *B. Ershler*

It was shown in the preceding communication that the curves showing the dependence of the capacity of a smooth electrode upon the potential as determined by the alternating current method, are somewhat different from the capacity curves obtained for the platinized electrode by the method described in parts I and III. The difference consists in a later rise of the capacity curve at anodic polarization and in an earlier rise when approaching the reversible hydrogen potential. We supposed in the same communication that the first difference may be caused by the slowness of the processes of deposition and removal of oxygen, and the second, by the presence on our smooth platinum of hydrogen more firmly bound than on platinized platinum.

In order to compare the properties of smooth and platinized electrodes it would be expedient to obtain for the former the same charging curves as were found in the above-mentioned work for the platinized electrode. The slow charging of the smooth electrode, however, possessing in general an insignificant capacity can be realized only with polarizing currents with densities of the order of 10^{-7} — 10^{-8} A, i. e. with densities which have the same order of

¹ A. Šlygin u. A. Frumkin, *Acta Physicochimica URSS*, **3**, 791 (1935). A. Šlygin, A. Frumkin u. W. Medwedowsky, *Acta Physicochimica URSS*, **4**, 911 (1936). A. Frumkin a. A. Šlygin, *Acta Physicochimica URSS*, **5**, 819 (1936). B. Ershler a. M. Proskurnin, *Acta Physicochimica URSS*, **6**, 195 (1937).

magnitude as the inevitable depolarization currents caused by traces of gases dissolved in the liquid².

The following scheme was proposed to carry out the slow charging of a smooth electrode. The electrode was charged in a very small volume of liquid which was very carefully isolated from the external air. All the oxygen present in this liquid could be easily removed by cathodic polarization of the electrode. The speed of the subsequent anodic depolarization was probably equal to the rate of diffusion of the oxygen through the ground joint of the cell into the liquid surrounding the electrode. This corresponded in our experiments to about $2 \cdot 10^{-10}$ amperes (see below) and thus the anodic depolarization currents could be neglected. The depolarization current caused by the evolution of hydrogen on approaching the reversible hydrogen potential for this electrode is limited by the volume of the liquid surrounding the electrode, since after saturation of the liquid with hydrogen to the concentration corresponding to the given potential, the depolarization currents are obviously stopped. The quantity of dissolved hydrogen in the small volume of the liquid we could use can be compared with the capacity of the electrode at potentials differing from the reversible one by 30—40 mV. In the present work we give the results of the experiments undertaken with this electrode.

Experimental part

The cell consisted of a capillary *b* (Fig. 1) 1.1 mm in diameter, widened at the end where a carefully ground joint *c* was inserted. A small platinum wire *d* was sealed into the bottom of the capillary, making contact with the electrode in the capillary to be investigated. A platinum wire *f* (1.03 mm in diameter and 24.6 mm in length) served as this electrode. The surface of the electrode amounted to 0.78 cm²; the values of the charging currents given in this paper were recalculated so as to correspond to a surface equal to one cm². The capillary was filled with the liquid by means of a special pipette, and then the electrode was intro-

² A smooth platinum electrode, for example, placed in a liquid through which nitrogen carefully purified from oxygen (with copper gauze and hydrosulfite) had been bubbled, could not take up a potential of about 0.1 Volt with respect to the reversible hydrogen electrode using polarizing currents with densities of $3 \cdot 10^8$ A/cm². The potential of the electrode with such a polarization was in general unstable and from time to time underwent unexpected and rapid changes of 0.1—0.2 V towards the anodic side. These fluctuations are evidently caused by convection currents in the liquid containing traces of oxygen.

duced. The latter fell freely and settled down on the wire *d*. The vessel was then tightly closed by the ground joint *c*. The volume of the liquid surrounding the electrode was not more than 5–6 mm³. The end of the siphon from the large hydrogen electrode *B*, with respect to which the potential of the electrode investigated was measured, and through which the polarization was effected, was introduced in the cup of the cell (Fig. 2). The resistance of the liquid in the ground joint was $0,5 \cdot 10$ ohms.

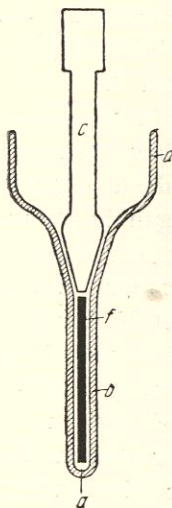


Fig. 1.

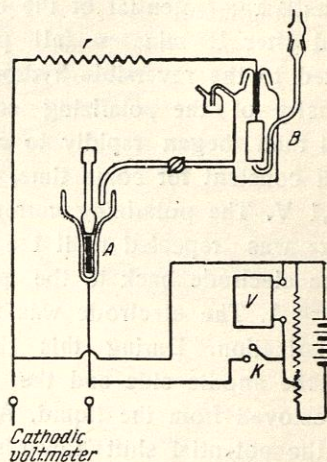


Fig. 2.

It was thus necessary to add to the potential measured during polarization of the electrode a correction for the drop of the voltage of the order of a few mV. This correction was measured separately. For the measurement of the potential of the electrode, a cathodic voltmeter was used; the measurement of the potential could be carried out to within 1–2 mV, and the amount of electricity drawn out during each measurement did not exceed 0,008 micro-coulombs. The diagram of the whole apparatus is shown in Fig. 2. *A* is the cell investigated, *B* is the hydrogen electrode, *r* is a resistance equal to $282 \cdot 10^6$ ohms and *V* is a voltmeter. The required potential was applied to the voltmeter with the aid of a potentiometer, and then, to start the polarization, the switch *K* was closed. The polarizing current is equal to $\frac{v + v_1}{r}$, where *v* is the voltage shown by the voltmeter, *v*₁ is the potential difference between the investigated electrode and the hydrogen electrode, and $r = 282 \cdot 10^6$ ohms.

The experiments were carried out in the following way. The electrode was purified by heating in *aqua regia*, then heated to

incandescence with a blast lamp and after cooling was dipped into the cell. The cell was tightly closed by means of the ground joint, and the electrode was subjected to cathodic polarization with a current density of 10^{-6} A. In the first moment of polarization the potential of the electrode rapidly fell, then this falling off slowed down³. For a certain time the potential remained almost constant and finally began to fall rapidly again. The polarization was prolonged until the potential of the electrode fell below 0,1 V, which happened after 18 minutes (all potentials given here and below are related to the reversible hydrogen potential in the same liquid). The density of the polarizing current was then decreased. The potential then began rapidly to change towards the anodic side, remained constant for some time, and then began to return to the value 0,1 V. The polarizing current was again decreased and this procedure was repeated until the polarizing current necessary to bring the electrode back to the potential of 0,1 V became smaller than 10^{-8} A. The electrode was then left for several hours without polarization. During this time the potential shifted a little towards the anodic side and the last traces of oxygen were evidently removed from the liquid. After such a treatment, the velocity of the potential shift towards the anodic side extraordinarily decreased. In the course of 24 hours such an electrode with a potential of 0,1 V in 1 N KBr shifts 20 mV to the anodic side. The capacity of the electrode studied by us at such a potential in this solution being equal to 800 microfarads, the depolarizing current in our cell amounted only to

$$\frac{800 \cdot \frac{20}{1000} \cdot 10^{-6}}{24 \cdot 60 \cdot 60} \cong 0,2 \cdot 10^{-10} \text{ A.}$$

Directly after this treatment the determination of the charging curve was carried out. For this purpose the electrode was brought to a potential of 0,087 V⁴ and, after maintaining it for some time at

³ The falling down is caused by the removal of the oxygen dissolved in the liquid and bound to the surface of the Pt.

⁴ We chose 0,087 V as the initial potential in order to completely eliminate the influence of hydrogen dissolved in the liquid on the value of the measured capacity. The electrical equivalent of the quantity of hydrogen saturating the whole volume of the liquid in our cell is less than 0,6 microcoulombs under these conditions.

this potential, the anodic polarization was started. The potential of the electrode was measured after definite intervals of time, equal to a few minutes. The anodic current was usually equal to $3,47 \cdot 10^{-8} \text{ A}$.

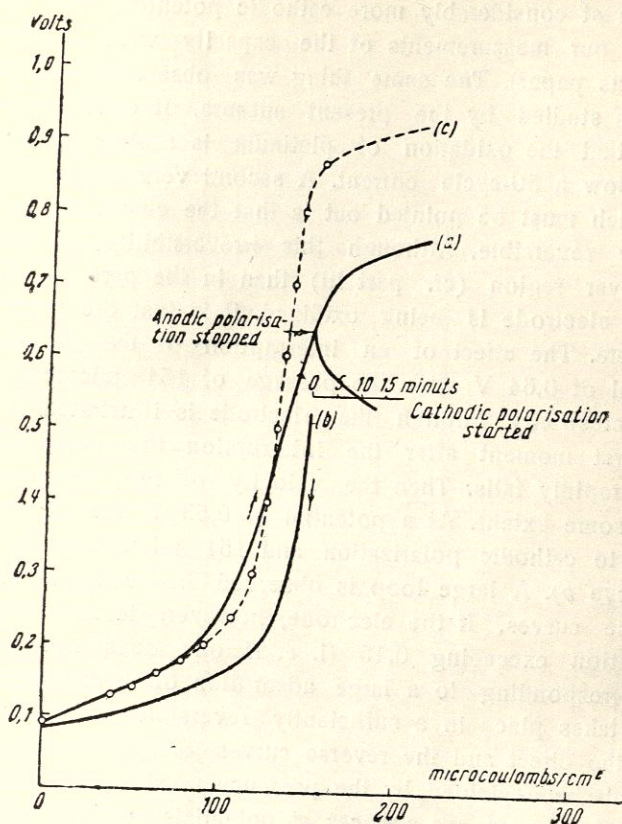


Fig. 3.

with this current the whole curve was determined in 2—3 hours; the quantity of electricity which passed through the electrode was computed by multiplying the current by the time which elapsed since the beginning of polarization.

Experimental results for 1N KBr + 0.03N HCl.

The most detailed studies were performed with this electrolyte; the charging curve is given in Fig. 3 (curve a). This curve is similar to the corresponding one, found for platinized platinum.

(curve *c*)⁵. First of all it is necessary to point out, that the bend in the curve *a*, corresponding to the beginning of oxidation of the smooth platinum (or to the beginning of adsorption of bromine), takes place at considerably more cathodic potentials than we could infer from our measurements of the capacity with 50 hertz a. c. (cf. previous paper). The same thing was observed with the other electrolytes studied by the present authors. It obviously follows from this that the oxidation of platinum is a slow process which cannot follow a 50-cycle current. A second very important circumstance which must be pointed out is that the charging curve is not completely reversible. Although this irreversibility is less in the double layer region (cf. part III) than in the part of the curve where the electrode is being oxidized, it is just the same clearly evident here. The effect of an interruption of the polarization at a potential of 0,64 V after the passage of 151 microcoulombs of positive electricity through the electrode is illustrated in Fig. 3. In the first moment after the interruption the potential of the electrode rapidly falls. Then the velocity of this falling off slows down to some extent. At a potential of 0,53 V the electrode was subjected to cathodic polarization and 151 microcoulombs passed again (curve *b*). A large loop is observed between the direct and the reverse curves. If the electrode, however, is not subjected to a polarization exceeding 0,15 (i. e. if one does not leave the region corresponding to a large adsorption of hydrogen) then the charging takes place in a sufficiently reversible way and the loop between the direct and the reverse curves disappears. The irreversibility can be explained by the presence of still noticeable quantities of hydrogen on our surfaces at potentials corresponding to the double layer region. This hydrogen is evidently held on the surface simply because the process of its deposition and removal proceeds slowly. It is removed, therefore, with the current densities which we used at potentials more anodic than the equilibrium potentials. The difference between the slopes of the direct and reverse curves in the double layer region may be explained in this way (the reverse curve has here a slope 2—3 times less than the

⁵ The scale of the curve for platinized platinum has of course been changed so as to make a comparison between the two curves possible.

direct one). It is interesting to note that in the case of the platinized electrode the difference between the slopes of the direct and reverse curves does not exceed 30—40%.

Several phenomena, however, which take place at potentials within the double layer region, cannot be wholly explained by the presence of bound hydrogen which is not in equilibrium with the solution at these potentials. These phenomena which bear witness to the finite and indeed sufficiently low speed of the processes taking place during the charging of the electrode in this region, may be described in the following way.

1. If the electrode is polarized to 0,5—0,6 volts starting with a potential of 0,1 V, and then the polarization is interrupted, the potential spontaneously decreases. This is obviously explained by the presence on the surface of hydrogen not in equilibrium, which is gradually removed from the surface and discharges the electrode. But if the electrode is polarized cathodically after a considerable halt at 0,5—0,6 V to 0,4—0,3 V, and then the polarization is stopped, the potential begins to change towards the anodic side; it is impossible to explain this phenomenon by the presence of non-equilibrium hydrogen bound on the surface of the electrode.

2. Comparing the capacity curve determined with alternating

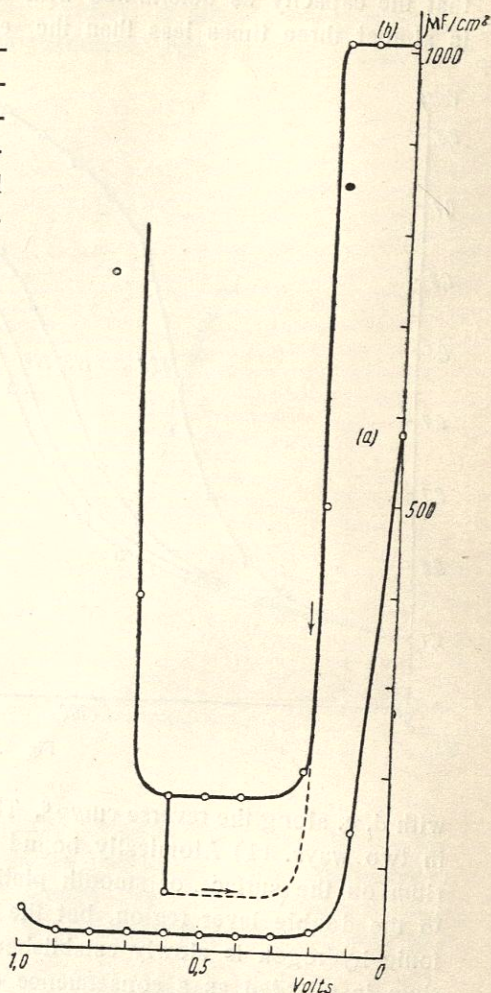


Fig. 4.

current (Fig. 4a) and the capacity curve computed from the reverse charging (the curve *b*, dotted part) for the same electrode, we find that the capacity as determined with a. c. in the double layer region is almost three times less than the equilibrium capacity measured

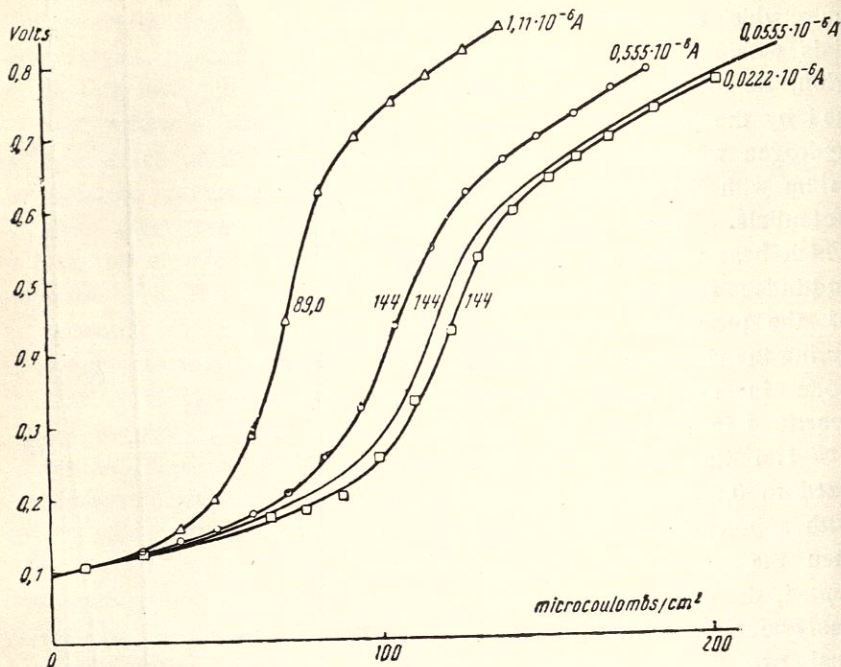


Fig. 5.

with d. c. along the reverse curve⁶. These phenomena can be explained in two ways. (1) Atomically bound hydrogen is present in equilibrium on the surface of smooth platinum at potentials corresponding to the double layer region, but the equilibrium between atomic and ionic hydrogen is slowly established. (2) The approach to equilibrium is retarded as a consequence of the finite velocity of charging of the double layer. Such a phenomenon would be possible, for example, with a non-uniform surface in the presence of obstacles for the motion of adsorbed ions on the surface. The data given in the present work evidently do not make it possible to interpret in an unambiguous way the slowness of the approach to equilibrium in the double layer region.

The very striking difference between the platinized and smooth electrodes consists in that the ratio of the capacity in the region of hydrogen adsorption to the capacity in the double layer region is considerably higher for the platinized than for the smooth electrode (20 and 8 respectively for curves *c* and *a* in Fig. 3).

This is, however, only an apparent difference. The charging curve for the platinized electrode indeed almost corresponds to equilibrium states as is proved by its reversibility. The curves of the smooth electrode, especially in the double layer region, are clearly irreversible. If the equilibrium value (i. e. the value computed from the reverse course of the curve *b*,

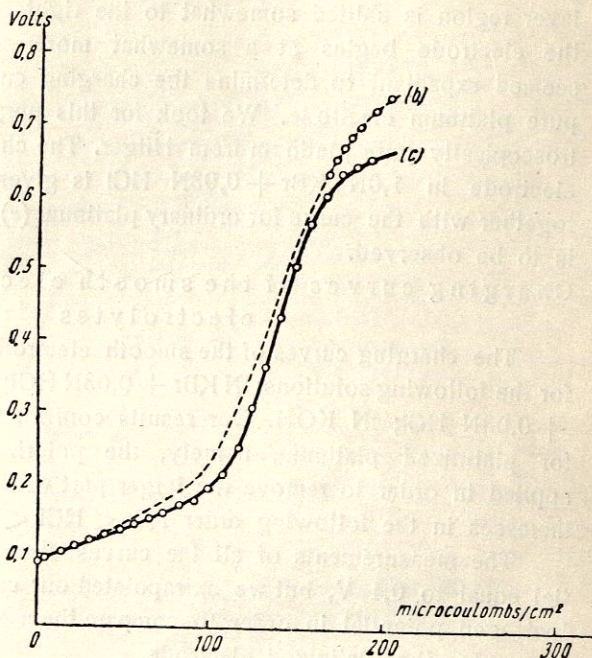


Fig. 6.

see footnote ⁶), is taken for the capacity in the double layer region, approximately the same value for the above-mentioned ratio on smooth platinum as on platinized platinum is obtained. Besides, it is evident from Fig. 3 that the

⁶ The direct and reverse courses of the charging curve have slopes differing from each other almost by a factor of 3. If during the cathodic polarisation, however, the potential is not brought to a value where the slow falling-off of the curve begins, and the anodic polarization of the electrode is again started, the slope of the curve of direct charging thus obtained nearly coincides with the slope of the reverse curve. This leads to the conclusion that the slope of the reverse curve nearly corresponds to equilibrium conditions during the charging. This difference also bears evidence of the fact that equilibrium is only slowly approached during the charging of the electrode in the double layer region, and in any case is not established when 50 cycle a. c. is used.

reverse curve for the smooth electrode is quite similar to the charging curve of the platinized electrode. The influence of the strength of the polarizing current on the form of the charging curve is shown in Fig. 5. This influence is similar to that observed for platinized platinum, namely, as the speed of charging decreases the double layer region is shifted somewhat to the right, and the oxidation of the electrode begins at a somewhat more cathodic potential. It seemed expedient to determine the charging curve for an especially pure platinum electrode. We took for this purpose a wire of spectroscopically pure platinum from Hilger. The charging curve for this electrode in 1,0N KBr + 0,03N HCl is given in Fig. 6 (curve *b*) together with the curve for ordinary platinum (*c*); no marked difference is to be observed.

Charging curves of the smooth electrode in various electrolytes

The charging curves of the smooth electrode are given in Fig. 7 for the following solutions: 1N KBr + 0,03N HCl; 1N HCl; 1N Na_2SO_4 + 0,03N HCl; 1N KOH. Our results confirm those already obtained for platinized platinum, namely, the polarization which must be applied in order to remove the larger part of the hydrogen absorbed increases in the following order $\text{KBr} < \text{HCl} < \text{Na}_2\text{SO}_4 < \text{KOH}$.

The measurements of all the curves were started from a potential equal to 0,1 V, but we extrapolated our curves to the reversible hydrogen potential in order to compare them with the corresponding curves for the platinized electrode.

The question concerning the amount of hydrogen capable of being adsorbed on 1 cm^2 of the surface of platinum at the reversible hydrogen potential presents a special interest. If we use the charging curve of the smooth electrode and assume that the region of hydrogen adsorption ceases where the curve begins to rise sharply and that the capacity of the double layer remains approximately constant independently of the potential, then in order to find the quantity of electricity, equivalent to the amount of hydrogen adsorbed at the reversible hydrogen potential, the linear part of the charging curve, which corresponds to the double layer region, must be prolonged until it intersects the axis of abscissae. The intercept on the axis of abscissae will obviously be equal to this quantity. This intercept for KBr corresponds to 218 micro-coulombs, which means $1,33 \cdot 10^{15}$ hyd-

rogen atoms per cm^2 . This is close to the number of platinum atoms on 1 cm^2 of a crystalline surface. In this instance we thus have an approximately monoatomic covering of the platinum surface by hydrogen. A. Frumkin and A. Šlygin found in part III a value for the covering of the surface of platinized platinum by hydrogen,

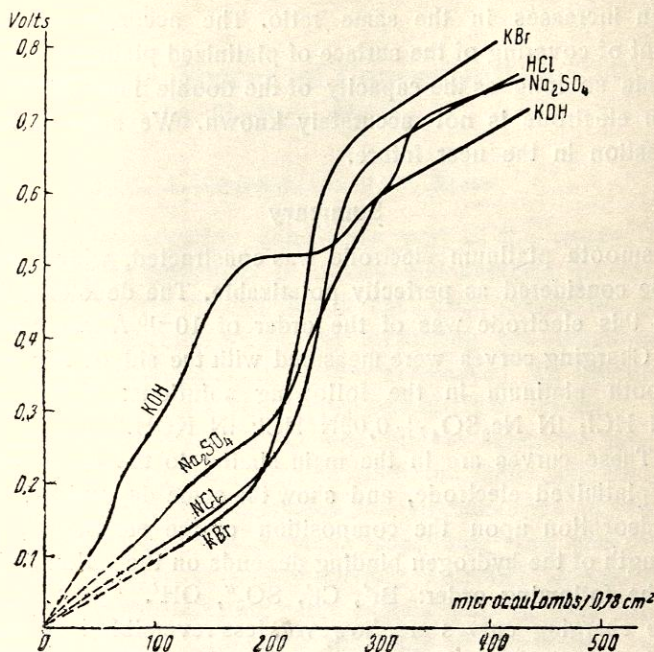


Fig. 7.

which was four times smaller, namely, $0.3 \cdot 10^{15}$ atoms per cm^2 . This discrepancy is explained by the method of calculation of the true surface of platinized platinum, which was used in this work. The magnitude if the true surface was calculated from the ratio of the capacities of the smooth and platinized electrodes at potentials corresponding to the double layer region, the quantity 20 microfarads per cm^2 found during the measurements with alternating current being used as the value of the capacity of the smooth electrode. It is evident from the present work that the true capacity of the double layer on smooth platinum may not be equal to this magnitude but can be considerably greater. In particular, the capacity computed

from the reverse course of the charging curve in KBr, which more nearly corresponds to equilibrium, is equal to 70 microfarads at potentials within the double layer region. If this quantity is taken as the basis for the calculation of the true surface of the platinized electrode, then the size of this surface is decreased by a factor 3,5 and the calculated degree of covering of the surface by adsorbed hydrogen increases in the same ratio. The accurate calculation of the extent of covering of the surface of platinized platinum will remain impossible so long as the capacity of the double layer of the smooth platinum electrode is not accurately known. We hope to return to this question in the near future.

Summary

A smooth platinum electrode was constructed, which practically could be considered as perfectly polarizable. The depolarization current for this electrode was of the order of 10^{-10} A per cm^2 .

1. Charging curves were measured with the aid of this electrode for smooth platinum in the following solutions: 1N KBr + 0,03N HCl; 1N HCl; 1N Na_2SO_4 + 0,03N HCl; 1N KOH.

2. These curves are in the main similar to the curves obtained for the platinized electrode, and show the same dependence of hydrogen adsorption upon the composition of the electrolyte, namely, the strength of the hydrogen binding depends on the anion and increases in the following order: Br' , Cl' , SO_4'' , OH' .

The charging curves are, however, less reversible than the curves obtained with the platinized electrode.

3. It was shown that slow processes take place on the electrode during its charging at potentials within the double layer region.

The possible significance of those processes is discussed.

4. The quantity of hydrogen atoms on 1 cm^2 of the surface of the smooth platinum electrode at the reversible hydrogen potential could be calculated. This quantity is nearly equal to the number of platinum atoms on the same surface.

I should like to take this opportunity to express my appreciation to Prof. A. Frumkin for many valuable suggestions during the course of this work.

Karpov Institute of Physical Chemistry,
Moscow.

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