The Polarization Capacity of a Smooth Gold Electrode

By *G. Deborin* and *B. Ershler*

In a series of recent investigations of the platinum electrode carried out under the guidance of Frumkin[1–10] it has been shown that with the help of polarization curves both the structure of the double layer at the electrode — solution interface and the rôle of the atoms adsorbed on the electrode in the establishment of the potential at this interface can be studied in detail. The polarization method, which has been worked out both for the platinized and for the smooth platinum electrodes, enables one to determine minute quantities of hydrogen or oxygen atoms adsorbed on the surface of the metal. This opens great possibilities in the study of the properties of metals in the cases in which the electrochemical behaviour is determined by the gases adsorbed on them. It is natural that the results obtained in the study of the platinum electrode have lead to the necessity of applying the theoretical and experimental material accumulated to the study of the

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1 Šlygin and Frumkin, Acta Physicochimica URSS, **3**, 791 (1935).
2 Šlygin, Frumkin u. Medwedowsky, Acta Physicochimica URSS, **4**, 911 (1936).
3 Frumkin and Šlygin, C. R. Acad. Sci. USSR, **2**, 176 (1934).
4 Ershler and Proskurnin, J. Phys. Chem. (Russ.), **8**, 689 (1936).
5 Ershler, Acta Physicochimica URSS, **7**, 387 (1937).
6 Ershler, Deborin and Frumkin, C. R. Acad. Sci. USSR, **5**, 1065 (1937).
7 Ershler and Frumkin, Trans. Farad. Soc., **31**, 4 (1939).
8 Dolin and Ershler, Acta Physicochimica URSS, in print.
9 Šlygin, Rasumovskaja and Rosental, J. Phys. Chem. (Russ.), **13**, 1079 (1939).
10 Ershler, J. Phys. Chem. (Russ.), **13**, 1092 (1939).

state of the surface for a number of other metals. We started with gold which is a representative of the group of metals for which the metal — solution interface potential is determined, over a wide range, by electrochemically active gases adsorbed on their surface and to which the methods worked out for platinum can be fully applied.

The adsorption properties of the surface of gold have scarcely been investigated directly. It is possible, however, to get an idea of the adsorption of hydrogen and oxygen on gold on the basis of certain indirect data.

The study of the gold electrode has hitherto been connected mainly with the question of its anode passivity. In a number of investigations by Shutt and Walton, Müller and others[11—21] the behaviour of the gold anode in different electrolytes and the influence of different factors on its passivity have been studied in detail. Although the views as to the mechanism of the anode passivity held by different authors are somewhat divergent, nevertheless it is universally assumed that the passivity of the gold anode is due to an oxide film which is formed on its surface at sufficiently high anodic potentials. In these investigations the gold was polarized by large current densities up to a considerable anodic potential, so that the state of the electrode surface was remote from equilibrium. Applying to gold a method worked out by them for platinum, Armstrong, Butler and Himsworth[22—23] showed that the formation of oxides begins at a definite potential and that in the case of basic solutions after prolonged polarization the degree of oxidation of the electrode does not exceed that which corresponds to a monolayer of oxygen atoms on the surface. They also showed that a preliminary treatment of the electrode

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[11—14] Shutt and Walton, Trans. Farad. Soc., **23**, 740 (1932); **30**, 914 (1934); **31**, 636 (1935); **29**, 1209 (1933).
[15] Shutt and Stirrup, Trans. Farad. Soc., **34**, 806 (1930).
[16] Pearson and Butler, Trans. Farad. Soc., **28**, 471 (1932).
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[18] Müller and Low, Trans. Farad. Soc., **26**, 635 (1930).
[19] Cohen u. Jacobson, Z. anorg. Chem., **55**, 321 (1907).
[20] Jirsa u. Jellinek, Z. Elektrochem., **30**, 286 (1924).
[21] Jirsa u. Bryanek, Z. Elektrochem., **29**, 126 (1923).
[22] Armstrong and Butler, Trans. Farad. Soc., **30**, 1173 (1934).
[23] Armstrong, Butler and Himsworth, Proc. Roy. Soc., **143**, 89 (1934).

essentially influences its subsequent polarization, which is in agreement with earlier investigations of Just and Beresowsky[24].

Great interest is presented by the investigations of the overvoltage of hydrogen on gold. Pring[25] and later Volmer and Wick[26] obtained on gold a reversible hydrogen electrode and, by measuring the overvoltage of hydrogen, showed that on gold it is larger than on platinum and copper.

By a direct action of atomic hydrogen on gold foil Pietsh and Josephy[27] succeeded in obtaining a visually observable white hydride. This hydride can exist but a short time at room temperature in air and in a hydrogen atmosphere.

Some idea of the adsorption capacity of the surface of gold can be obtained from a study of its catalytic properties. In the case of gold the latter are, however, expressed very weakly. Gold does not catalyze the hydrogenation reactions at all. According to some authors[28], this is explained by the fact that gold does not give unstable intermediate compounds with hydrogen. Among other catalytic reactions on gold we may quote: the decomposition of ammonium[29], hydrogen iodide[30] and hydrogen peroxide[31], and the oxidation of carbon monoxide[32]. In the present work the method of polarization capacity was used for the investigation of the properties of the surface of gold in electrolytic solutions, which fills certain gaps in our knowledge of the properties of the gold electrode.

Experimental part

The polarization measurements on a smooth gold electrode were carried out by a method described before[5] and used for the study of the polarization capacity of a smooth platinum electrode. Fig. 1 shows the cell which was used in our measurements. In contradistinc-

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[24] Just u. Beresowsky, Z. Elektrochem., **15**, 297 (1909).
[25] Pring, Z. Elektrochem., **19**, 255 (1913).
[26] Volmer u. Wick, Z. physik. Chem., **172**, 429 (1935).
[27] Pietsh u. Josephy, Naturwiss., **19**, 737 (1931).
[28] Green, "Industrial Catalysis", Macmillan (1928).
[29] Dulomg and Thenard, Ann. chim. physique, **23**, 440 (1823).
[30] Hinshelwood and Prichard, J. Chem. Soc., **127**, 1553 (1935).
[31] Weiss, Trans. Farad. Soc, **31**, 1547 (1935).
[32] Finch and Stimson, Proc. Roy Soc., **144**, 320 (1934).

tion to the earlier designs of this apparatus the present cell was provided with two ground glass joints between which the electrode investigated was situated in a capillary. The siphon of a large hydrogen electrode, serving as a reference electrode, is dipped into the solution of the electrolyte surrounding the upper ground glass joint *A*, that is, in the cup *C*. The lower end of the cell rests on the bottom of a cup filled with the solution of the electrolyte. The cup is connected (also with the help of a siphon dipped into the cup *E*) with another hydrogen electrode used for polarization. The introduction of the second ground glass joint *B* which means division of functions of the auxiliary electrode and the reference electrode, enabled us to avoid the introduction of corrections for the potential drop in the ground glass joint and at the same time ensured easy washing of the capillary by streaming water.

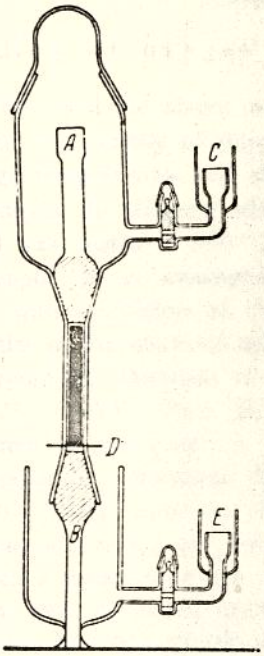

Fig. 1. Cell for electrode polarization.

A spectroscopically pure gold wire (Haereus) about one mm. in diameter, with an apparent surface of 0.72 cm.^{2}, was used as electrode. It was pressed against a thin platinum wire *D* sealed along the diameter of the capillary and serving for leading the current to the electrode. The measurements of the potential relative to a reversible hydrogen electrode in the same solution were carried out with the help of a quadrant electrometer with an accuracy to 2—3 mV. The polarization measurements were carried out, as a rule, with a current of 1.6×10^{-7} A.

The solutions of the electrolytes were prepared from carefully purified Kahlbaum reagents and were subjected to prolonged purification on a large, freshly platinized platinum electode in a hydrogen atmosphere. Just before the experiment the hydrogen was removed from the solution by a flow of nitrogen passed through a liquid air trap for purification. Before each experiment the electrode was cleaned

by etching in hot aqua regia with subsequent multiple washing in conductivity water.

Experimental results

Binding of oxygen on gold at high temperatures

We used the above method in the first place for the determination of the quantity of oxygen which is bound on the surface of gold at high temperatures, and also of those potentials at which this oxygen is removed in different electrolytes. For this purpose the gold wire tested was heated at 900° C for five minutes in a quartz tube in air, whereupon in an atmosphere of nitrogen it was dipped into a cell filled with a solution of the electrolyte saturated with nitrogen. The potential of the electrode treated in this way (with reference to a reversible hydrogen electrode in the same solution) is approximately equal to 0.75—0.95 V. Then the electrode was cathodically polarized with a current of 1.6×10^{-7} A. The cathodic polarization of the electrode to a potential exceeding that of the reversible hydrogen electrode by 50—70 mV. requires 1000 microcoulombs. The remainder of the oxygen, which had not been removed from the surface of the electrode at such a polarization rate, was removed from it by subsequent polarization with a smaller current density. To obtain a stable electrode potential near that of the reversible hydrogen potential an additional amount of electricity totalling 200 microcoulombs was required. The total quantity of electricity passed during the cathodic polarization of the electrode was equal to 1200 microcoulombs. The amount of oxygen bound on the electrode in five minutes at 900° C (reckoned per 1 cm.^{2} of the apparent surface of the electrode) is thus equivalent to 1700 microcoulombs. This corresponds to

$$\frac{1}{2} \frac{1700 \times 6.06 \times 10^{23}}{96\,480 \times 10^6} = 5.33 \times 10^{15}$$

oxygen atoms per 1 cm.^{2} of the apparent surface of the electrode, that is, approximately to four atomic layers of oxygen, if it is assumed that the number of gold atoms per 1 cm.^{2} of the apparent surface of the electrode is equal to 1.262×10^{15}.

Fig. 2 represents the cathodic polarization curves of a gold electrode oxidized at a high temperature, in different electrolytes.

The potentials relative to a reversible hydrogen electrode in the same solution are plotted as ordinates, while the quantity of electricity in microcoulombs per cm.^{2} of the apparent surface of the electrode, as abscissae. The curves show plainly that the potential required for

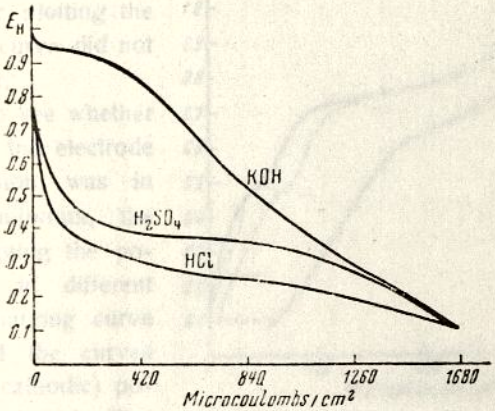

Fig. 2. Curves of the cathodic polarization of an oxidized gold electrode.

the removal of oxygen is very different in bases and acids. In acids it is more cathodic than in bases, which means that the binding of oxygen by the surface of gold is stronger in the former than in the latter. The fact that the oxygen film is more easily removed in bases is in full agreement with the results (see below) of the measurements of the polarization capacity, which show that the oxygen film is more readily formed in acids than in bases. These two facts point to the capacity of the oxidized gold surface to bind anions. Similar phenomena are known for gold sols in which oxychlorides are formed on the surface of the particles.

The charging curves of the gold electrode

The charging curves of gold electrodes were investigated in special detail in a 1N solution of H_2SO_4. The measurement of these curves

was commenced directly after the removal, by means of polarization, of all the oxygen adsorbed by the electrode in air. Then the electrode was kept for some time at a potential exceeding that of the reversible hydrogen electrode by 50—70 mV. whereupon anodic polarization began. The potential of the electrode was measured every minute. With a current density equal to 2.2×10^{-7} A/cm.^{2}, the time required for plotting the whole charging curve did not exceed one hour.

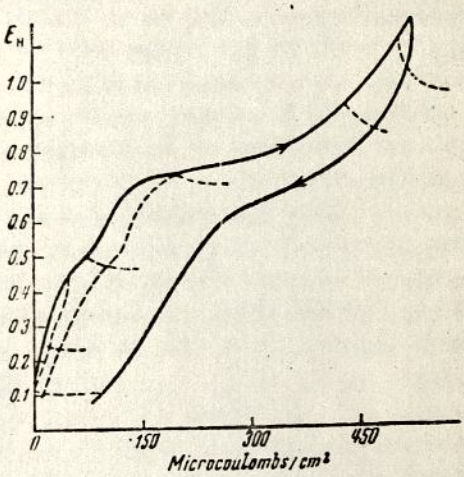

Fig. 3. Charging curves in 1 N H_2SO_4.

In order to see whether the surface of the electrode during polarization was in a state of equilibrium, the effect of interrupting the polarizing current in different parts of the charging curve was studied, and the curves of the reverse (cathodic) polarization were plotted. The results obtained enable us to draw certain conclusions as to the state of the electrode at different potentials.

The curve shown in Fig. 3 is typical for a 1 N solution of H_2SO_4.

It can be easily calculated from this curve that the total amount of electricity required for changing the potential of the electrode from a value approximately equal to that of the reversible hydrogen electrode to a value close to a reversible oxygen potential, is equal to 430 microcoulombs. At the very beginning of the curve (up to a potential of 0.28 V.) the direct course of the curves fully coincides with the reversed one and, after the interruption of the polarizing current, the potential undergoes no considerable variation with time[33].

The interruption of the polarizing current at higher anodic potentials is accompanied by larger variations of the potential and by an

[33] The variation of potential with time after the interruption of the polarizing current is shown by dotted horizontal lines.

increase of the hysteresis loop between the cathodic and anodic polarization curves[34]. These phenomena show beyond doubt that at sufficiently high anodic potentials the state of the surface of the electrode greatly deviates from equilibrium. Similar phenomena have been previously investigated in detail by Šlygin[1] in the case of a platinized platinum electrode and by Ershler[5] in the case of a smooth platinum electrode. It has been shown by these authors that the deviation from the equilibrium state, and in particular the appearance of a hysteresis loop between the anodic and the cathodic branches of the polarization curves, is connected with the beginning of the oxidation of the electrode. The velocity of this process is, as is well known, extremely small; the formation of the oxide film, therefore, lags behind the variation of the electrode potential, which gives rise to a hysteresis loop. It must be assumed that in the case of the gold electrode the appearance of the large hysteresis loop between the anodic and the cathodic branches of the polarization curves is due to the oxidation of the surface of the gold electrode. In this case the halt of the potential at 0.75—0.85 V. must be ascribed to an oxygen film. The removal of oxygen bound by gold in air at 900° C takes place, as has been shown above, at lower potentials, which points to a stronger binding of this oxygen by the surface of gold. According to these curves, the amount of bound oxygen varies between 0.5 and 1 atomic layer. It must also be noted that the linear portion of this halt corresponds to a narrower potential range than in the case of platinum. The linear portion of the curve is followed by a more rapid rise.

The arrest of the anodic curve situated at potentials 0.45—0.55 V. can be due, generally speaking, both to adsorption of hydrogen and to adsorption of oxygen. This question cannot be decided quite unambiguously with the help of the above methods alone. A somewhat greater reversibility of this part of the curve leads to assume that this arrest is due to the hydrogen, which is very firmly bound on the electrode surface. The length of this arrest is equivalent to fifty microcoulombs, which corresponds approximately to 0.3 atomic layer of hydrogen as reckoned with respect to the apparent electrode surface.

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[34] In Fig. 3 the cathode curves plotted from 0.45 and 0.73 V. are shown by dotted lines.

Assuming that this stop is actually due to the hydrogen bound on the electrode, it must be noted that this hydrogen is bound by the surface very firmly, for it can only be removed at potentials of 0.4—0.5 V. with reference to the reversible hydrogen electrode. The passivity of hydrogen bound on the surface of gold in different catalytic reactions is probably due to this strong binding.

The capacity of the first portion of the curve, where a rapid increase of potential with time is observed, is equal to 70 μF/cm.^{2} of the apparent electrode surface. If the surface of gold at these potentials is charged positively, the capacity of the double layer must be approximately equal to this value. If, however, the surface is negatively charged, the capacity of the double layer must be several times smaller. This portion of the curve must therefore correspond, according to the position of the zero point of the charge of the gold surface, either to a complete absence of hydrogen on gold or the presence of a certain amount of hydrogen, which is removed (deposited) uniformly throughout this range of potentials.

Influence of oxidation on the shape of polarization curves

Repeated measurements of polarization curves have shown that unless the surface of the electrode is specially standardized before the experiment, it is impossible to obtain reproducible curves, their shape becoming gradually more distorted. In other words the history of the electrode, and in particular the degree of its preliminary oxidation, essentially influences the shape and length of the charging curve which is obtained after the removal of the oxygen bound on the electrode surface as a result of its oxidation.

Fig. 4 shows a series of charging curves in a 1 *N* solution of H_2SO_4, each successive curve referring to an electrode which was subjected to a more prolonged oxidation than the preceding one. The ordinates represent the same quantities as in the previous figures. The longest charging curve *I*, which has a long halt at potentials 0.73—0.8 V., was obtained after heating the electrode in a hydrogen atmosphere. The electrode treated in this way, without contact with air, was dipped in a hydrogen atmosphere into a cell filled with a solu-

tion saturated with hydrogen. Curve *II* refers to an electrode oxidized at 900° C in air during five minutes, curve *III* — 15 min., curve *IV*— 30 min. and curve *V*—120 min. In all these cases the hydrogen in the electrolytic solution was preliminarily supplanted by nitrogen which

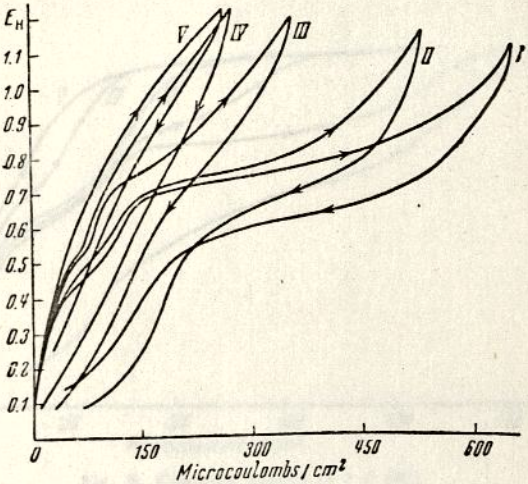

Fig. 4. Charging curves in 1 *N* H_2SO_4.

was cleaned by passing through a spiral tube of a liquid air trap. The transfer of the electrode into the cell was also carried out in a nitrogen atmosphere. Fig. 5 shows similar curves for a 1 *N* solution of HCl, and Fig. 6., for a 1 *N* solution of KOH.

The curves in Figs. 4, 5, 6 show that the length of the charging curve decreases as the degree of preliminary oxidation of the electrode is increased; in the first place decreases the length of the oxygen arrest at 0.7—0.75 V. and vanishes the arrest at 0.45—0.55 V. The charging curve of a gold electrode heated in air at 900° C for two hours is nearly linear throughout its length and is characterized by complete absence of any arrests. The whole range of potentials can be gone through in this case with 120—150 microcoulombs. A return to the initial shape of the polarization curve is only possible when the electrode is heated long enough at 800—900° C in a hydrogen stream. The electrode treated in this way gives again a charging

curve identical with curve *I* and lends itself to the whole cycle of measurements described above.

Heating in hydrogen thus constitutes the standard treatment of the electrode, which enables one to obtain reproducible results.

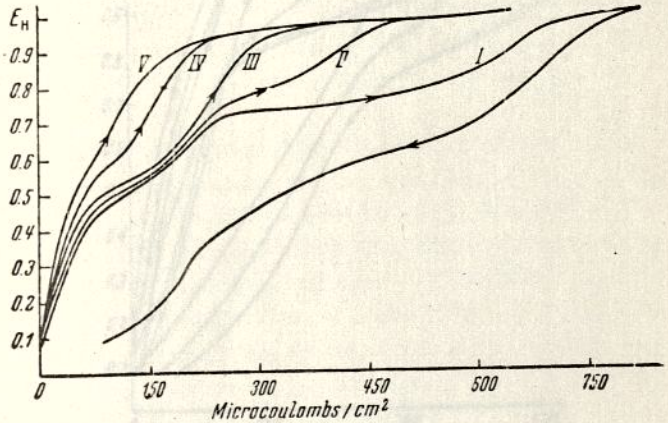

Fig. 5. Charging curves in 1 *N* HCl.

The phenomenon referred to above and consisting in a distortion of the shape of the charging curves with the degree of preliminary oxidation of the electrode can be explained as follows.

When gold is heated in air, its surface becomes covered by firmly bound oxygen which is not removed during the cathodic polarization of the electrode up to the reversible hydrogen potential. The amount of this firmly bound oxygen increases with increase of the oxidation time, and only a prolonged heating of the electrode in a hydrogen flow reduces the oxide film which is covering it. The oxygen firmly bound on the surface of the electrode fills it up as a result of which the adsorption capacity of the electrode for other gases is found to be decreased for subsequent measurements of the charging curves. The conditions of treatment of the electrode before the experiment thus constitute the decisive factor which determines the length and the shape of the charging curves. From this point of view the

relatively small adsorption capacity of gold under ordinary conditions is due, apparently, to the "poisoning" of its surface by firmly bound oxygen.

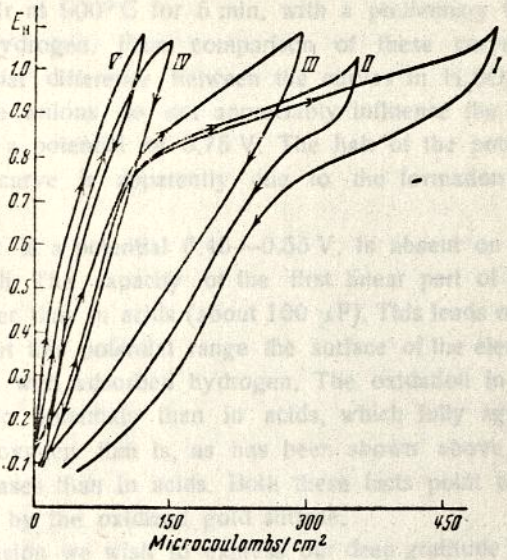

Fig. 6. Charging curves in 1 *N* KOH.

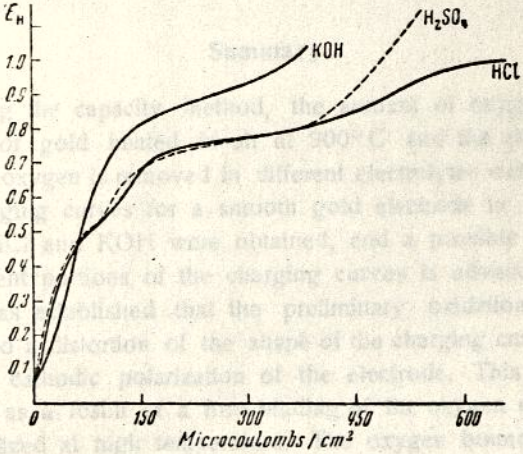

Fig. 7. Charging curves of gold electrode in different electrolytes.

The charging curves of a gold electrode in different electrolytes are compared in Fig. 7.

All the curves plotted in Fig. 7 were obtained after heating the electrode in air at 900° C for 5 min. with a preliminary heating of the electrode in hydrogen. From comparison of these curves it follows that no essential difference between the curves in H_2SO_4 and HCl is observed. The anions do not appreciably influence the shape of the curves up to a potential of 0.75 V. The halt of the potential at 1 V. on the HCl curve is apparently due to the formation of a surface oxychloride.

An arrest at a potential 0.45—0.55 V. is absent on the charging curve in alkali. The capacity of the first linear part of the curve is, however, larger than in acids (about 100 μF). This leads one to suppose that throughout this potential range the surface of the electrode is probably covered with adsorbed hydrogen. The oxidation in alkali begins at more anodic potentials than in acids, which fully agrees with the fact that the oxygen film is, as has been shown above, more easily removed in bases than in acids. Both these facts point to the binding of the anions by the oxidized gold surface.

In conclusion we wish to express our deep gratitude to Prof. A. N. Frumkin for his constant interest in our work and for his participation in the discussion of its results.

Summary

1. Using the capacity method, the amount of oxygen bound on the surface of gold heated in air at 900° C and the potential range in which this oxygen is removed in different electrolytes were determined.

2. Charging curves for a smooth gold electrode in 1 *N* solutions of H_2SO_4, HCl and KOH were obtained, and a possible interpretation of the different portions of the charging curves is advanced.

3. It was established that the preliminary oxidation of the electrode leads to a distortion of the shape of the charging curves obtained after careful cathodic polarization of the electrode. This phenomenon is explained as a result of a firm binding of the oxygen on the surface of gold oxidized at high temperature. The oxygen bound in this way cannot be removed on subsequent cathodic polarization of the electrode till the reversible hydrogen potential. This leads to a decrease in the

capacity of the surface of the gold electrode to bind gases during subsequent anodic polarization.

4. The amount of oxygen deposited during anodic polarization on the electrode surface which is cleaned to a large extent from the firmly bound oxygen, varies between 0.5 and 1 atomic layer; in their anodic portion the curves differ essentially from platinum by the fact that their linear part corresponds to a narrower potential range (especially in acids) and is followed by a steeper rise.

5. The oxygen bound on the gold surface is more easily removed in bases than in acids and is less easily deposited in bases, which points to a binding of the anions by the surface oxides of gold. With an increase in the preliminary oxidation of the surface of gold the adsorption of oxygen during anodic polarization becomes more difficult.

6. The potential arrest at 0.45—0.55 V. can be ascribed to hydrogen or oxygen. If it is assumed that this arrest is due to the presence of hydrogen, the latter must be bound on the gold surface very firmly. Its quantity amounts to 0.3 atomic layer. This arrest corresponds to a narrower potential range than the hydrogen arrest in the case of platinum.

7. The anions have no appreciable influence on the slope of the charging curves at potentials near the reversible hydrogen potential.

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