The Anodic Oxidation of Metals at Very Low Current Density. Part V. Gold.*

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The results of various workers on the variation of the anode potential with the quantity of electricity passed when the gold electrode is forced from hydrogen to oxygen evolution, as well as on the type of oxide formed on the surface of the metal before oxygen evolution, are not in agreement. These are clarified in this investigation by studying the anodic oxidation of gold in acid, neutral, and alkaline solutions at very low current density. It is shown that Au_2O is first formed on the anode, then AuO, and lastly Au_2O_3 before oxygen evolution. No evidence has been obtained for the presence of the oxide AuO_2.

The results of various workers on the anodic oxidation of gold as well as the type of oxides formed on the surface of the metal before oxygen evolution are not in agreement. Jeffery (*Trans. Faraday Soc.*, 1915, **11**, 9), studying the electrolysis of nitric, sulphuric, and orthophosphoric acids with gold anodes, reported separation of a brown mixture of hydrated Au_2O and Au_2O_3. Jirsa and his co-workers (Jirsa and Buryanek, *Chem. Listy*, 1922, **16**, 189, 299, 328; *Z. Elektrochem.*, 1923, **29**, 126; Jirsa and Jelinek, *Chem. Listy*, 1924, **18**, 1; *Z. Elektrochem.*, 1924, **30**, 286, 534) showed that Au_2O, Au_2O_3, and AuO_2 were formed on gold anodes in solutions of sulphuric acid. The dissociation pressure of the oxide AuO_2 was considered to be above 1 atm., so that it liberated oxygen and formed Au_2O_3. Shutt and his co-workers (Shutt and Stirrup, *Trans. Faraday Soc.*, 1930, **26**, 635; Shutt and Walton, *ibid.*, 1932, **28**, 740; 1933, **29**, 1209; 1934, **30**, 915) found that when gold was anodically polarised in sulphuric acid Au_2O_3 was formed, but in hydrochloric acid Au_2O_4 was the only oxide formed. The thickness of the oxide film in both cases was 1—2 molecules. Armstrong, Himsworth, and Butler (*Proc. Roy. Soc.*, 1933, **143**, *A*, 89), using moderate current densities and a string galvanometer as an indicating instrument, found that in 0·1M-sulphuric acid there were two stages in the polarisation—the first rapid, linear change was attributed to the charging of a double layer, and the second, gradual rise of potential starting from +1·27 v was considered to represent the formation of auric oxide initially as a unimolecular layer. In 0·1M-sodium hydroxide the stages were less distinct, but from the quantity of electricity passed, it was concluded that at a potential of ~+0·5 v the adsorption of a single layer of oxygen atoms took place.

Deborin and Erschler (*Acta Physicochem. U.S.S.R.*, 1940, **13**, 347), on the other hand, concluded that the anodic oxidation of a gold surface leads to the formation of a layer of 0·5—1 oxygen atom adsorbed on the surface. Hickling (*Trans. Faraday Soc.*, 1946, **42**, 518), using his oscillographic method, showed that Au_2O_3 was formed as a unimolecular film on the surface of the anode before oxygen evolution.

We have now studied the anodic oxidation of gold at very low current density in acid, neutral, and alkaline solutions, and show that Au_2O is first formed on the anode, followed by AuO and then Au_2O_3 before evolution of oxygen. No evidence has been obtained for the presence of the oxide AuO_2.

* Part IV, preceding paper.

Experimental

The electrical circuit and the electrolytic cell employed were as described by El Wakkad and Emara (*J.*, 1952, 461; 1953, 3504, 3508). The gold anode was prepared by electrodeposition from a cyanide bath, prepared by dissolving 1 g. of pure auric chloride in 6 times the quantity of potassium cyanide solution necessary for its conversion into the complex cyanide. The total volume was then made up to 500 c.c. The electrodeposition was carried out by a current of 20 mA per electrode for 3 min. on a platinum foil 1 × 1 cm. to give it a smooth coating. The current was then raised to 430 mA per electrode, and the electrodeposition continued for a further 10 min. to give a spongy deposit with a large surface. The electrodeposition was carried out between 55° and 60°. The prepared electrode was washed several times in conductivity water and then with the solution under investigation before it was introduced into the electrolytic cell. Each experiment was carried out with a freshly prepared electrode. The anode was placed in such a position with respect to the cathode as to ensure uniform distribution of the polarising current at the anode surface. The cathode was a platinum wire 2 cm. long and 0·1 cm. in diameter.

Measurements were carried out mainly in the following solutions: 0·1N-sulphuric acid, 0·2M-KH_2PO_4 + 0·2M-Na_2HPO_4 buffer mixture of approximate pH 6·8, 0·1M-sodium carbonate solution of pH 11·5, and 0·1N-sodium hydroxide, all prepared from " AnalaR " materials and conductivity water. The solution was boiled before use and cooled in an atmosphere of pure nitrogen to remove any dissolved oxygen.

The polarising currents used were 150 μA per electrode in sulphuric acid and phosphate buffer, and 10 and 300 μA in sodium carbonate solution and sodium hydroxide solution, respectively. In each solution three studies were carried out on each electrode—the anodic polarisation, the cathodic polarisation, and the anodic decay. The procedure adopted in obtaining the corresponding curves was as described before (El Wakkad and Emara, *J.*, 1952, 461). The reference half-cell was a saturated calomel electrode prepared as described before (*idem, loc. cit.*). The electrolytic cell and the reference half-cell were kept in an air thermostat at 25°±0·01°. The E.M.F. was measured with a Tinsley potentiometer and a mirror galvanometer. All potentials quoted are on the hydrogen scale.

Measurements of the Oxide Potentials of Gold.—The only oxide the existence of which has been completely established is Au_2O_3. On the other hand, preparation of Au_2O and AuO has often been claimed (Kruss, *Ber.*, 1886, **19**, 2541; *Annalen*, 1887, **237**, 241; Pollard, *J.*, 1926, 1347; Buchrer, Wartman, and Nugent, *J. Amer. Chem. Soc.*, 1927, **49**, 1271; Steigmann, *Chem.-Ztg.*, 1926, **50**, 595; Part, *Compt. rend.*, 1870, **70**, 842; Dudley, *Amer. Chem. J.*, 1902, **28**, 61; Schottlander, *Annalen*, 1883, **217**, 312; Gerke and Rouske, *J. Amer. Chem. Soc.*, 1927, **49**, 1855).

Owing to the extreme instability of aurous oxide, we intended to measure its potential at the moment of its formation against a gold electrode. A tall beaker of *ca.* 100 ml. capacity was fitted with a rubber bung having openings for a gold electrode, a syphon for the calomel electrode, inlet and outlet for nitrogen, and an opening for the nozzle of a burette. About 50 ml. of 0·01N-sodium hydroxide solution were placed in the beaker, boiled, and cooled in an atmosphere of pure nitrogen.

Aurous chloride, prepared by reduction of chloroauric acid with sulphurous acid (Pollard, *loc. cit.*), was allowed to drop from the burette. To ensure the absence of any oxide on the surface of the gold electrode, it was cathodically polarised and the current was interrupted directly before measurements.

For the preparation of the bivalent gold oxide we used the method of Kruss and Dudley (*locc. cit.*). Pure gold wire (0·88 g.) was dissolved in aqua regia, and the solution evaporated to dryness. A small amount of water was added and evaporated, and the process was carried out three times to eliminate nitric fumes. The crystals of gold chloride were taken up in the minimum amount of water, and auric oxide precipitated by addition of dilute sodium hydroxide at the b. p. of the solution, " AnalaR " sodium chloride being added to prevent formation of colloidal hydroxide. The oxide was dried and then heated at 160° in an air-oven to constant weight. The oxide potential measurements were carried out in 0·1N-sulphuric acid and in 0·1N-sodium hydroxide with a gold electrode.

Results and Discussion

Curves *A*, Figs. 1, 2, and 3, represent the characteristic anodic polarisation curves of gold at 25° in 0·1N-sulphuric acid, in phosphate buffer of pH 6·8, and in 0·1M-sodium carbonate solutions. The polarising currents were 150 μA per electrode in the first two

solutions and 10 μA per electrode in the last. From these curves, which show the variation of the potential of the gold electrode as it is forced from the hydrogen- to the oxygen-evolution potentials, it can be seen that there is a rapid initial build-up of potential which can be attributed—by analogy with the previous studies (El Wakkad and Emara, *loc. cit.*)—to the charging of the double layer. This is followed by three well-defined arrests before oxygen evolution. For the determination of the capacity of the double layer in this case, polarisation was carried out at extremely low current densities, *viz.*, 10 μA per electrode in both the sulphuric acid and the phosphate buffer, and 5 μA per electrode in the carbonate solution. Measurements from a large number of polarisation curves at such very low

FIG. 1.

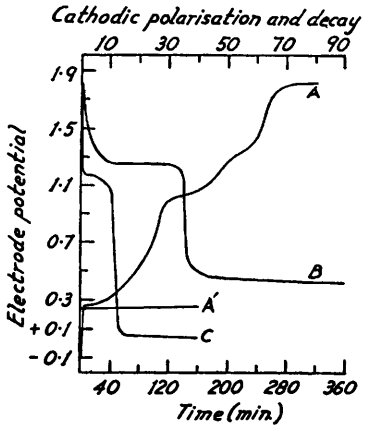


FIG. 2.

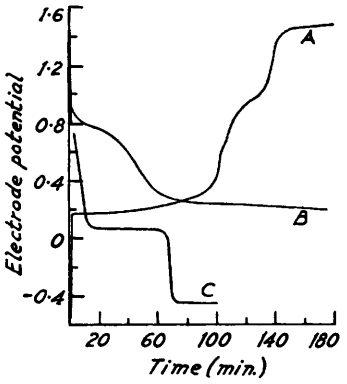


FIG. 3.

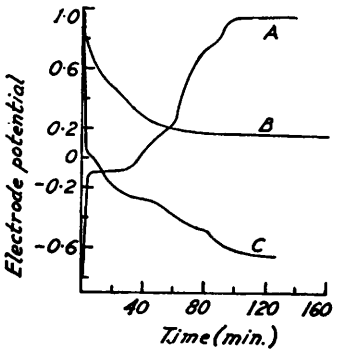
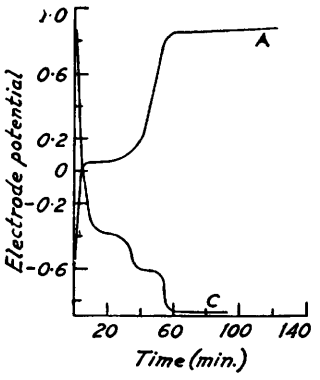


FIG. 4.



current densities gave an average value for the double layer capacity in 0·1N-sulphuric acid of about 2000 μF per electrode; in the phosphate buffer (pH 6·8) the average value was of the same order, but in 0·1M-sodium carbonate solution it was about 2500 μF per electrode.

The first step after the charging of the double layer appears to start at a potential of +0·27 v in 0·1N-sulphuric acid, and −0·05 and −0·25 v in the phosphate and carbonate solutions respectively. The last two values were obtained from charging curves carried out at extremely low current densities, *viz.*, 10 and 5 μA per electrode, for the determination of the capacity of the double layer as was stated before. The second step appeared to start at potentials of +0·96, +0·62, and +0·15 v in the three solutions respectively. The third step starts at potentials of +1·26, +0·86, and +0·70 v in the acid, neutral, and alkaline solutions, respectively.

Oxide Potentials of Gold.—In the Au–Au_2O system, the potential recorded within 20 sec. was −0·3 v, which changed towards a more positive value, becoming +0·60 v

after about 2 min. where it remained constant. The pH value of the hydroxide solution after the formation of the oxide was 12·0. If the potential recorded within the first 20 sec. is considered to represent a rather rough measure for the potential of the system Au–Au_2O, then $E°_B$ (the potential at the extreme alkaline range of pH) of the reaction $Au + 2OH^- = Au_2O + H_2O + 2e$ will be about −0·42 v. The rapid increase in the potential observed experimentally may be readily explained on the basis of the instability of the aurous oxide which decomposes rapidly into Au_2O_3 and gold. This is confirmed by the fact that the final potential recorded experimentally gives an $E°_H$ value (potential value at the extreme acid range of pH) for the system Au–Au_2O_3 of 1·32 v, in very good agreement with results obtained by Gerke and Rourke (*loc. cit.*), Buehrer and Roseveare (*J. Amer. Chem. Soc.*, 1927, **49**, 1989), and Hickling (*loc. cit.*).

In the Au–AuO system, a constant potential of +0·98 v was recorded in 0·1N-sulphuric acid from the beginning of the experiment and remained constant for over 6 hr. In 0·1N-sodium hydroxide solution the potential recorded was +0·27 v at first; it then drifted until it reached 0·41 v within one hour, where it remained constant.

In the following Table, the starting potentials of the three steps observed in the anodic polarisation curves are compared with the equilibrium potentials of the systems Au–Au_2O, Au–AuO, and Au–Au_2O_3 at the corresponding pH values.

	Starting potentials (v):			Equilibrium potentials (v) of the system:		
Solution	First step	Second step	Third step	Au–Au_2O	Au–AuO	Au–Au_2O_3
0·1N-H_2SO_4	+0·27	+0·96	+1·26	+0·36	+0·98	+1·30
Phosphate buffer ...	−0·05	+0·62	+0·86	0·00	+0·62	+0·94
0·1M-Na_2CO_3	−0·25	+0·15	+0·70	−0·24	(+0·38)	+0·70

The agreement between the starting potentials of these steps and the equilibrium values for the three systems (except for the value in parentheses, see p. 3102) strongly suggests that these three steps observed in the anodic polarisation curves correspond to the consecutive formation of Au_2O, AuO, and Au_2O_3 on the gold anode before evolution of oxygen.

The fact that in this case the agreement is between the starting potentials and the metal–metal oxide potentials and not between the oxidation–reduction potential of the higher and lower oxides as always found in previous studies (El Wakkad and Emara, *locc.cit.*) can be explained by the instability of the lower oxides, for it is well known that Au_2O and AuO are unstable in aqueous solutions (Pollard, *loc. cit.*; Jirsa and Buryanek, *loc. cit.*), decomposing to Au_2O_3 and gold.

The instability of the aurous ion in aqueous solutions is also obvious from the fact that the standard potentials of the systems $Au \longrightarrow Au^+ + e$ and $Au \longrightarrow Au^{3+} + 3e$ are *ca.* 1·68 v and *ca.* 1·42 v, respectively (Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," New York, 1938, p. 182), which shows that the potential of the Au–Au^+ system is more positive than that of the Au–Au^{3+} system, indicating the instability of the former.

The quantity of electricity passed in the first step in the case of the carbonate solution was about 15,000 μC. This is sufficient for the liberation of about $4·65 \times 10^{16}$ oxygen atoms. The specific gravity of gold being taken as 19·3, the diameter of the gold atom may be calculated as $2·6 \times 10^{-8}$ cm., and hence there would be about $1·5 \times 10^{15}$ atoms of gold per true sq. cm. A rather rough estimate for the ratio of the real to the apparent area of our gold electrode may be obtained from the capacity of the double layer. The capacity of the anodic double layer before oxide formation as obtained from previous studies (El Wakkad and Emara, *loc. cit.*) can be estimated as 100 μF per true sq. cm. If the difference between the capacity of our gold electrode and that for the true sq. cm. is assumed to be due only to the difference in the surface area, the ratio of the real to the apparent area will be about 12·5, and the true surface area of our gold electrode will be about 25 sq. cm. This value gives about $3·75 \times 10^{16}$ gold atoms on the surface of our electrode. This shows that the quantity of electricity passed in the first step corresponds to the formation of an Au_2O film about 2 molecules thick. It must be emphasised that these results are very approximate owing to the instability of this oxide in aqueous solutions, as was shown before. The quantity of electricity passed in the second step was about 15,000 μC per

electrode, suggesting that the film of AuO is also about 2 molecules thick, and similarly from the third step it appears that the film of AuO was further oxidised to Au_2O_3, *i.e.*, the film of Au_2O_3 is also about 2 molecules thick. These results for the thickness of Au_2O_3 on the gold anode before oxygen evolution are in agreement with those obtained by Shutt and Walton (*loc. cit.*).

In 0·1N-sulphuric acid solution, the quantity of electricity passed in the first step was about 315,000 μC, *i.e.*, sufficient for the liberation of $9{\cdot}76 \times 10^{17}$ atoms of oxygen. The ratio of the real to the apparent area being taken as 10 (from capacity measurements), there will be 3×10^{16} gold atoms on our electrode. This result indicates that the oxide film in this case is 32 molecules thick. This very high value suggests that the oxide in such solution is somewhat more soluble than in the carbonate solution. In order to test this assumption, the behaviour of the gold anode in 9N-sulphuric acid was studied. The result, shown in curve *A'*, Fig. 1, indicates that when the gold anode was polarised in such a strong acid solution, the potential did not rise to the oxygen-evolution value but remained constant at the Au–Au_2O potential, thus confirming our view. From this behaviour, the standard condition ought to be that of the carbonate solution.

The behaviour of gold in 0·1N-sodium hydroxide solution, Fig. 4, is somewhat different from that in all the other solutions, for in this case one step was recorded, which began at about −0·2 v when an extremely low polarising current (10 μA per electrode) was used, and at about +0·00 v at 300 μA per electrode before oxygen evolution.

This anomalous behaviour of gold in such alkaline solutions was noticed also by most of the previous authors (Armstrong, Himsworth, and Butler; Hickling, *locc. cit.*), and it seems to be due to the amphoteric character of the gold oxides which form aurite and aurate in such strong alkaline solutions. This fact may explain also the difference between the potential of the second step in the carbonate solution and that for the Au–AuO system.

The cathodic curves *C*, Figs. 1—3, show reduction steps at the Au_2O_3 potential at the corresponding pH values, and another step at the Au–Au_2O potential before hydrogen evolution. The existence of the first step is in accordance with the fact that Au_2O_3 was formed on the electrode during the anodic polarisation. The presence of the second step is unexpected owing to the instability of aurous oxide as was shown before. Hickling (*loc. cit.*) observed the same step during his oscillographic study of the gold electrode. Several experiments on the cathodic polarisation of the gold anodes showed that this step always appeared in the neutral and the carbonate solutions, whereas in acid solutions its appearance depended upon the experimental conditions such as the polarising current density during the anodic polarisation and the duration of the anodic polarisation at the oxygen-evolution potential. These facts seem to indicate, as suggested by Hickling (*loc. cit.*), that this arrest observed during the cathodic polarisation was due to oxygen in the solution formed during the anodic polarisation. As will be seen from the discussion of the decay curves, the oxygen may originate also from the decomposition of Au_2O_3. As this step always takes place at the Au–Au_2O potential at the corresponding pH values, it seems that the oxygen reacts first with the gold to give Au_2O, which is then reduced by cathodic current to the metal before hydrogen evolution. There is no step corresponding to the reduction of the AuO oxide in any of the solutions.

The decay curves *B*, Figs. 1—3, show a step at the potential of Au_2O_3 at the corresponding pH values, after which the potential of the gold electrode fell to a value slightly more positive than that of the Au–Au_2O system. There is no step corresponding to the decomposition of AuO. These results suggest that the higher oxide Au_2O_3 is unstable in contact with the metal, which is in accordance with the previous findings in all the metals studied (El Wakkad and Emara, *loc. cit.*; Tourky and El Wakkad, *J.*, 1948, 740, 749; El Wakkad, *J.*, 1950, 3563). The fact that the potential became constant at a value more positive than that of the Au–Au_2O system is quite in harmony with the fact that Au_2O is unstable, decomposing to gold and Au_2O_3, and since the latter is also unstable in contact with the metal, one must expect that the potential of the electrode will be intermediate between the values of the systems Au–Au_2O and Au–Au_2O_3 as found experimentally.

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