The Anodic Behaviour of Gold

PART II — OXIDATION IN ALKALINE SOLUTIONS

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The dissolution of gold in alkaline solutions containing cyanide ions is of great importance and its application in the MacArthur-Forrest process towards the end of the last century revolutionized the extraction of gold from its ores. Because of this, and its use in many industrial processes involving gold, it has been widely studied. What is known — and still unknown — about this reaction constitutes the main theme of this second instalment of a review of the anodic behaviour of gold.

Part I of this review (40) dealt with the anodic characteristics of gold in acidic solutions containing various ligands which form stable complexes with gold(I) or gold(III). The kinetics and mechanisms of the formation of oxide films on gold by anodic polarization were discussed, as well as the various theories regarding the chemical nature of the films and the influence that their formation has on the anodic dissolution and passivation of the metal. In those cases for which data were available, the mechanisms of the active dissolution of the metal were reviewed and its behaviour in the presence of various ligands was discussed with special reference to the proportions of gold(I), gold(III) and the oxidized forms of the ligands which are produced by anodic polarization at various potentials. Part II deals with the corresponding reactions of gold in alkaline solutions.

Thermodynamic Aspects

Thermodynamic data relevant to the anodic behaviour of gold were summarized in Figures 1 and 2. In regard to these, points to be noted as relevant to reactions at high pH values are the following:

- (1) The potential required for the formation of Au_2O_3 (or other gold oxides) decreases with increasing pH, as does that for the oxidation of water to oxygen (Figure 1)
- (2) The chemical equilibria involving the gold complexes are (within the stability range of the ligands) uninfluenced by changes in pH in the alkaline region. Thus the data summarized in Figure 2 are independent of pH
- (3) Points (1) and (2), considered together, indicate that oxide formation (and therefore passivation) can be expected to reduce the number of ligands

that can be used in alkaline, as opposed to acidic, solutions for the active dissolution of gold. In fact, the only ligand of any significance is cyanide

- (4) In strongly alkaline solutions, gold can be expected to dissolve as the HAuO_2^- ion (Figure 1).

Oxidation in Non-Complexing Media

As discussed in Part I, the oxidation of gold in aqueous solutions containing no additional complex-forming species generally results in its passivation via the formation of oxide films on the surface. A general

Fig. 11 Cyclic voltammograms for the oxidation of gold in 0.1 M potassium hydroxide and in 1 M perchloric acid. The abscissa scales are of different sensitivities as well as laterally displaced to allow the curves to overlap and to demonstrate their general similarity

Fig 12 Current against potential curves for the oxidation of gold in alkaline cyanide solutions

1	0.077 M CN^- , pH 12	after (43)
2	0.1 M CN^- , 0.1 M OH^-	after (46)
3	0.2 M CN^- , pH 12.8	after (50)
4	0.04 M CN^- , pH 12	after (51)
5	0.5 M CN^- , 55°C	after (48)
6	0.1 M CN^- , pH 11	after (45)
7	0.2 M CN^- , 0.2 M OH^- , 61°C	after (49)

Solution temperatures, unless otherwise stated are approximately 20°C

overview of the formation and properties of these films was given and much of this can be expected to apply equally well to the anodic behaviour of gold in alkaline solutions. However, relatively little has been published relating specifically to the electrochemistry of gold at high pH values.

Thacker and Hoare (41), in studying the use of gold as a reference electrode material, observed no change in the appearance of the electrode surface during anodization at a low current density in potassium hydroxide solutions. The major process apparently taking place was the evolution of oxygen, accompanied by a slight dissolution of gold (presumably as the aurite ion), as evidenced by the faintly yellow colour of the solution after 24 hours. At high current density, a visible dark red oxide layer was also formed, which dissolved under open-circuit conditions, leaving a bright gold surface.

El Wakkad and Shams el Din (42) found three potential arrests during the anodic polarization of electrodeposited gold electrodes at low current densities in 0.1 M sodium carbonate solution, but only one arrest at about 0.05 V in 0.01 M sodium hydroxide solution. These results were interpreted in terms of the successive formation of Au_2O , AuO and Au_2O_3 on the electrodes in the sodium carbonate solution and of the formation of AuO on them in the sodium hydroxide solution.

Cathro and Koch (43), however, observed only one potential arrest with massive gold electrodes in 0.1 M sodium carbonate solutions and concluded that the use of electrodeposited gold electrodes, containing occluded cyanide ions, was responsible for the anomalous results which were reported by el Wakkad and Shams el Din.

A cyclic voltammogram obtained in the writer's laboratory at a gold electrode in 0.1 M potassium hydroxide is shown as the solid curve in Figure 11. The voltammogram is very similar to that observed in an acid solution (shown as the dotted curve), but is, as predicted on thermodynamic grounds (Figure 1), shifted to more negative potentials with increasing pH. The actual shift of about 0.9 V for the cathodic peak is close to that predicted, namely 0.78 V. It would therefore seem that the single oxide Au_2O_3 , which was found to be formed in acid solutions, is also responsible for the passivation behaviour in alkaline media.

Recent work by Arvia's group (44), however, has shown that the oxidation of gold in alkaline solutions is a more complex process. By employing rapid-sweep cyclic voltammetry they were able to observe the reversible oxidation and reduction of gold in sodium hydroxide solutions at potentials below the reversible potential for the $\text{Au}/\text{Au}_2\text{O}_3$ couple, that is in the region of ~ 0.3 to 0.2 V. This they interpreted as be-

ing due to the formation of a monolayer of adsorbed Au(OH). At higher potentials, they found several anodic and cathodic peaks which they suggested could be associated with different gold(III) surface species. As in the case of the oxidation of gold in acidic solutions (17), they observed changes in the curves with increasing sweep rate, which indicated that structural and chemical changes in the oxide film were occurring during oxidation and reduction.

Oxidation in Cyanide Solutions

The most stable complexes of gold(I) and gold(III) are those that are formed with the cyanide ion (Figure 2). It is therefore not surprising that the majority of industrially important processes involving gold in solution are based on the use of cyanide. In particular, most of the baths used in the gold-plating industry contain the aurocyanide ion as the active species. Equally significant is the almost universal use of cyanide solutions to effect the dissolution of gold from its ores. As first demonstrated by Kudryk and Kellogg (45), this is an electrochemical process in which the anodic dissolution of gold is accompanied by the cathodic reduction of oxygen. Much has been published on the chemistry of this process, but relatively little of the literature has dealt in any detail with the anodic reaction which, as will be demonstrated below, is complex.

Experimental Observations

Examination of the data point for cyanide in Figure 2 shows that, in contrast to the other ligands, the cyanide complex of gold(I) is more stable than that of gold(III) by as much as 0.5 V. It is therefore not surprising that most authors have simply assumed that the stoichiometry of the anodic dissolution reaction in cyanide solutions is:

This has been supported by the coulometric measurements of Kudryk and Kellogg (45) who did not, however, specify the potentials at which their experiments were conducted. Kirk *et al.* (46, 47) carried out a large number of carefully controlled coulometric experiments in solutions containing 0.1 M KOH and 0.1 M KCN. They concluded that the electrochemical dissolution of gold in alkaline cyanide is a one-electron transfer reaction throughout the potential range of -0.65 to 0.55 V. At higher potentials, there was evidence of the formation of gold(III) species. Eisenmann (48) also ascribed the increased currents at potentials above 0.4 V to the formation of gold(III).

The current against potential behaviour of gold in cyanide solutions has been studied by a number of authors and the lack of general agreement is apparent from the curves shown in Figure 12. The data most

amenable to comparison, referring to similar, though not identical, experimental conditions were selected from various original publications (43, 45 to 51). Examination of the curves shows that, with only one exception, several peaks are obtained when the potential of a gold electrode in cyanide solutions is increased from -0.7 to 0.8 V. Kudryk and Kellogg (45), on the other hand, noted that the dissolution of gold was controlled by the diffusion of cyanide ions to the metal surface at potentials above about -0.1 V and found no evidence for passivation even at low concentrations of cyanide.

Despite the large variations in the relative heights of the peaks, there appears to be some agreement regarding their positions. They occur at potentials in the vicinity of -0.4, 0.3 and 0.6 V, and in experiments conducted at elevated temperatures, at 0 V. In no case, however, are more than three peaks observed and it could therefore be argued that the anodic oxidation of gold in cyanide solutions involves the formation of three passivating species.

The Effects of Heavy Metal Ions

Before discussing in detail the mechanisms of the dissolution and passivation of gold that have been proposed in the light of the general current *vs.* potential characteristics of Figure 11, it seems appropriate to speculate on the origin of the unusually wide scatter in the results obtained by the various workers.

Cathro and Koch (43) recognized this problem and referred to the work of Mills (52) and of Cathro (51) which had shown that the presence, even in very low concentrations, of heavy-metal ions such as those of lead, mercury, bismuth and thallium can have signifi-

Fig. 13 Effect of the addition of thallium ions on the current against potential curve for the oxidation of gold in 0.04 M cyanide solutions. After (51)

cant influence on the extent of passivation. The results of Cathro (51) on the effect of thallium ions on the peak at -0.35 V are shown in Figure 13. It is apparent that passivation, at least in the case of this peak, does not occur in the presence of thallium ions. Linear-sweep voltammetric curves for the anodic dissolution of gold in cyanide solutions, obtained in the author's laboratory, are shown in Figure 14. The pronounced effects of the addition of lead or mercury ions on the nature of the peak at 0.4 V are evident. It should also be noted that these additives appear to leave the anodic characteristics of gold at more positive potentials essentially unchanged.

It is perhaps relevant that the cathodic reduction of the $\text{Au}(\text{CN})_2^-$ ion is also influenced favourably by the presence of heavy-metal ions. As shown recently in the author's laboratory (53), this explains why the addition of lead nitrate is so effective in promoting the precipitation of gold by zinc dust from leach liquors in the cyanide process for the treatment of gold ores. McIntyre and Peck (54) made a detailed study of the depolarization effects induced by heavy-metal ions during the electrolytic deposition of gold from cyanide solutions. They showed that the trace additives which are most effective as depolarizers are

those that tend to deposit uniformly on a gold surface, thus forming an adsorbed monolayer at potentials positive to those at which their cathodic deposition as bulk metals begins, that is, at underpotentials. They concluded that the depolarization phenomenon is caused primarily by an enhancement of the rate of nucleation, stemming from the strongly adsorbed foreign metal atoms. In addition, catalytic electrochemical displacement (cementation) reactions are made possible by the fact that the exchange current densities of the various depolarizer couples are much greater than that of the $\text{Au}(\text{CN})_2^-/\text{Au}$ couple.

In view of these observations, it is not surprising that there is a general lack of agreement between the experimental results obtained by different workers. Because all the ions mentioned above (lead, mercury, bismuth and thallium) can be cemented out by gold in cyanide solutions, they are deposited on the surface of gold electrodes immersed in solutions in which they are present as trace impurities. Thus, Cathro and Koch (43) not only purified all their reagents by recrystallization, but also etched their electrodes in 1 M potassium cyanide for several hours before starting their experiments. These, however, consisted of steady-state potentiostatic measurements which re-

quired waiting times of up to 30 minutes to allow a steady current to develop at each potential. It is probable that, despite the earlier precautions, these lengthy periods at constant potential resulted in the contamination of the electrodes with lead (the most likely impurity). In the studies which yielded the data shown in Figure 12, no attempt was made to purify the solutions used and the inconsistency of the results may possibly be ascribed to the varying purity of the reagents and to differences in the experimental procedures. It is significant that in those studies which were based on steady-state potentiostatic measurements the peak at -0.35 V was noticeably higher, whereas that at 0.25 V was lower, than in those obtained by linear-sweep voltammetry.

Experiments carried out in this laboratory confirm that the presence of small amounts of impurities in the solutions used can have a pronounced effect on the anodic behaviour in the region of the peak at -0.4 V. Thus, the accumulation, by cementation, of heavy metals such as lead on the gold surface can be expected to increase with time and agitation under conditions of open circuit, when the potential is sufficiently cathodic (less than -0.7 V) for the reduction of the metal ions to be controlled by mass transport. The curves shown in Figure 15 demonstrate this point. A long period under conditions of open circuit and enhanced mass transport (achieved by rotating the gold electrode at $1\,000$ r/min) give rise to a large peak at -0.4 V, whereas a longer open-circuit period without rotation leads to a very much smaller peak. As in the case of the addition of lead and mercury ions (Figure 14), the influence on the more anodic peaks is relatively minor. A similar effect of electrode rotation on the peak at -0.4 V was observed, but not discussed, by Kirk *et al.* (46).

A further demonstration of the factors influencing the dissolution and deposition of gold is given by the cyclic voltammograms shown in Figure 16. These were recorded in the author's laboratory and confirm those of MacArthur (49), who observed a small cathodic peak at about -0.65 V during a cathodic sweep of the potential of a gold electrode in a solution containing aurocyanide ions. The curves shown in Figure 16 demonstrate that the peak occurs only in the presence of aurocyanide ions in solution, which can be introduced either by anodic dissolution or by direct addition. Further experiments have shown that the magnitude of the peak in aurocyanide-containing solutions increases with the addition of trace amounts of lead ions.

This discussion illustrates that the anodic dissolution of gold and its deposition from aurocyanide ions are both subject to passivation at potentials close to the equilibrium potential and that the presence of trace amounts of heavy-metal impurities in solution

can have a similar effect in reducing the extent of passivation. In view of these conclusions, any mechanism proposed for passivation during anodic dissolution should also accommodate the corresponding cathodic process.

Mechanisms of Dissolution and Passivation

The mechanism of dissolution and passivation in the region of each of the three main peaks, namely those at -0.4 , 0.3 and 0.6 V, are discussed in turn below.

The Peak at -0.4 V

On the basis of measurements of the current at various potentials on the active portion of the peak at -0.4 V, and of the variation in current with the concentration of cyanide at constant potential, Cathro and Koch (43) suggested the following mechanism for the dissolution reaction in this region:

The first step was considered to be rate-determining. An apparent decrease of the peak potential with increasing pH was interpreted in terms of the formation of a gold hydroxide or basic cyanide which caused passivation of the metal. However, as pointed out by MacArthur (49) and Kirk *et al.* (46), hydroxide formation is not possible at potentials as low as -0.4 V.

Fig. 16 Effect of electrode rotation and the addition of aurocyanide ions on the current against potential curves for the oxidation and reduction of a gold disc electrode in a solution containing 0.1 M KOH and 0.1 M KCN

Fig. 17 Comparison of the anodic behaviour of a rotating disc gold electrode in 0.1 M KOH with that in a solution of 0.1 M KOH and 0.1 M KCN. Note that in the latter case the current sensitivity was increased by a factor 10 during the reverse sweep

(The voltammogram in Figure 17 shows that oxide formation on a gold electrode occurs only at potentials above about 0.3 V). Furthermore, basic gold cyanides are not known to exist in alkaline cyanide solutions.

MacArthur (49) supported the view that oxidation proceeds through a surface intermediate, probably an adsorbed gold cyanide (AuCN_{ADS}) and that, when the surface is completely covered, the rate of the reaction is controlled by the rate of chemical dissolution of this intermediate, that is, passivation is caused by a layer of AuCN_{ADS} . Kirk *et al.* (46) did not propose a mechanism for dissolution and passivation in this region, although their mechanism for the other peaks involved an AuCN_{ADS} species. Eisenmann (48), in a study dealing primarily with the deposition of gold, also supported the view that oxidation and reduction occur through an adsorbed AuCN layer. On the basis of a few rather inconclusive experiments at various pH values, Pan and Wan (50) suggested, though without great conviction, that the adsorption of hydroxyl ions on the surface of the gold is the cause of the passivation.

Therefore, while it can reasonably be argued that some form of adsorbed AuCN is responsible for passivation of gold electrodes in the region of the peak at -0.4 V, it is not yet clear why electrodes of the other Group IB metals (silver and copper) do not exhibit similar behaviour in cyanide media. The role of heavy-metal impurities in preventing passivation when adsorbed on the surface of gold is likewise not resolved. An interesting clue to the possible nature of the adsorbed AuCN layer is to be found in the macromolecular structure of solid AuCN , which consists of linear chains in which the cyanide ion func-

tions as a bidentate ligand. It is conceivable that this type of structure could develop in two dimensions to form a passive layer on the surface. The presence of foreign heavy-metal atoms on the surface would be likely to disrupt the formation of such a layer, thereby reducing the extent of passivation. It is also possible that the co-deposition of the so-called 'polymer' together with gold from acid cyanide solutions containing cobalt or nickel (55) could be a related phenomenon.

The Peak at 0.3 V

Cathro and Koch (43) found that the height of the peak at 0.3 V did not show any reproducible trend with changes in cyanide concentration, but that its position was apparently independent of pH. They suggested that dissolution in this region occurs by the oxidation of a basic gold(I) cyanide to a basic gold(III) cyanide. However, as found by Kirk *et al.* (47), dissolution in this region occurs by one-electron oxidation, and cannot therefore be the result of the conversion of a gold(I) to a gold(III) species. The latter workers found that at low cyanide concentrations the dissolution rate at the peak increases approximately linearly with cyanide concentration, but decreases with increasing pH. At high concentrations of cyanide and hydroxide, the rate decreases with increasing cyanide concentration. On the basis of these results, they proposed that the second step in the following mechanism is rate-determining in the region of the peak at 0.3 V:

Because a one-electron transfer step is involved in this mechanism, it can explain the formation of one peak, but it cannot, by reasonable argument, be made to predict the appearance of *further* peaks.

The Peak at 0.6 V

There is general agreement that passivation at 0.6 V is caused by the formation of an oxide layer on the gold surface. This is illustrated in Figure 17, which shows voltammograms for a gold electrode in alkaline solutions with and without added cyanide. It is apparent that passivation occurs in the region in which the oxide forms, that is, above about 0.5 V, and that re-activation of the electrode on the reverse sweep occurs only at potentials below those at which the oxide is reduced. This behaviour parallels that discussed in Part I for the passivation of gold in halide solutions.

Cathro and Koch (43) found that the peak potential decreased with increasing pH, as predictable from Figure 1, for the potential required to form an Au_2O_3 layer. The peak height increased with increasing cyanide concentration and this was confirmed by Kirk *et al.* (46), who found a linear dependence of the maximum rate of dissolution on the concentration of cyanide. Cathro and Koch (43) offered no mechanism for the dissolution reaction in this region, whereas Kirk *et al.* (46) suggested that the last step in the mechanism proposed above is rate-determining. As already discussed, however, this explanation cannot accommodate *both* the peaks at 0.3 V and at 0.6 V. On the other hand, MacArthur (49), while conceding that the reaction was too complex to be analyzed fully, suggested that either direct oxidation of gold to $\text{Au}(\text{CN})_2^-$ without the formation of an adsorbed intermediate, or oxidation to gold(III), could account for dissolution in this region.

It should be apparent from this discussion that, despite a considerable research effort over many years, the mechanisms of the anodic dissolution and passivation of gold in cyanide solutions are still not adequately resolved and that much remains to be explained in this area. As already indicated, it is suspected that there are several important parallels between the dissolution and the deposition of gold, and further research should therefore be planned with this in view.

Oxidation in the Presence of Other Ligands

As far as the author is aware, there is no published information on the anodic dissolution of gold in alkaline solutions containing ligands other than cyanide. A possible reason for this, as stated earlier, is that oxide formation (and therefore passivation) is likely to prevent dissolution with most of the ligands

listed in Figure 2. It should, however, be mentioned that a potential ligand, the sulphide (or polysulphide) ion, does not appear in Figure 2 because of a lack of relevant thermodynamic data. The extraction of gold from arsenical concentrates using ammonium polysulphide solutions has nevertheless been described (56). Although this aspect is not specifically mentioned, the process presumably involves the anodic dissolution of gold to form polysulphide complexes by way of a mixed-potential mechanism.

Acknowledgement

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Electrical Resistivity of Gold

A DETAILED REVIEW OF DATA

A synthesis of 125 sets of experimental data on the electrical resistivity of gold has recently been published (*J. Phys. Chem. Ref. Data*, 1979, **8**, (4), 1147-1298) by R. A. Matula of the Center for Information and Numerical Analysis and Synthesis at Purdue University, West Lafayette, IN., U.S.A. Thus, recommended curves for the electrical resistivity of gold are presented for the temperature range 1 to 1740 K and recommended values for the total resistivity are tabulated for the same temperature range, while values of the intrinsic resistivity of gold between 15 and 1337.58 K (the melting point of gold) are also tabulated. The interest of Matula's authoritative work is greatly enhanced by a detailed description of his methodology and by clear information of the uncertainty in the published values. Similar work on copper, palladium and silver is presented in the same article.