

10–14 February, 2003

All that is Gold Does Not Glitter

The Italian Luigi V. Brugnatelli performed electrodeposition of gold in 1805, using the voltaic pile discovered by [Alessandro Volta five years earlier](#). Forty years later, John Wright of Birmingham, England, discovered that potassium cyanide was a useful electrolyte for gold and silver electroplating.

1. To prepare the solutions for gold electroplating, gold is dissolved in potassium cyanide (KCN) in air. Several redox reactions then occur in the highly basic media (pH 10–12.5). The first can be represented as: $\text{Au} + \text{CN}^- + \text{O}_2 \rightarrow [\text{Au}(\text{CN})_2]^- + \text{H}_2\text{O}_2$; what is the balanced equation (in basic solution)?

a) oxidation: (unbalanced) $\text{Au} \rightarrow [\text{Au}(\text{CN})_2]^-$; (balanced) $\text{Au} + 2 \text{CN}^- \rightarrow [\text{Au}(\text{CN})_2]^- + e^-$

b) reduction: (unbalanced) $\text{O}_2 \rightarrow \text{H}_2\text{O}_2$; (balanced) $2e^- + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 + 2 \text{OH}^-$

c) net: $2 \text{Au} + 4 \text{CN}^- + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 2 [\text{Au}(\text{CN})_2]^- + \text{H}_2\text{O}_2 + 2 \text{OH}^-$ (eq a must be multiplied by 2 before adding)

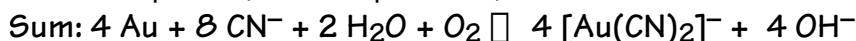
2. In a second step, more gold and cyanide react with the hydrogen peroxide generated in the first step; i.e., $\text{Au} + \text{CN}^- + \text{H}_2\text{O}_2 \rightarrow [\text{Au}(\text{CN})_2]^- + \text{OH}^-$; what is the balanced equation (in basic solution)?

a) oxidation: (unbalanced) $\text{Au} \rightarrow [\text{Au}(\text{CN})_2]^-$; (balanced) $\text{Au} + 2 \text{CN}^- \rightarrow [\text{Au}(\text{CN})_2]^- + e^-$

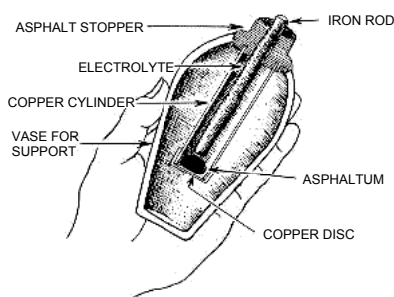
b) reduction: (unbalanced) $\text{H}_2\text{O}_2 \rightarrow \text{OH}^-$; (balanced) $2e^- + \text{H}_2\text{O}_2 \rightarrow 2 \text{OH}^-$

c) net: $2 \text{Au} + 4 \text{CN}^- + \text{H}_2\text{O}_2 \rightarrow 2 [\text{Au}(\text{CN})_2]^- + 2 \text{OH}^-$ (eq a must be multiplied by 2 before adding)

3. What is the net equation (sum of steps 1 and 2)?



4. Could electroplating have been achieved centuries before Brugnatelli's time? A 6-inch-high yellow earthenware jar discovered in 1936 in a village near Baghdad, Iraq, dates from the time of the Parthian Empire (247 B.C. to 224 A.D.). The jar contained a cylinder of sheet copper (in the lower left of the figure at right), and the bottom of the cylinder was capped with a crimped-in copper disk and sealed with bitumen (asphalt). Another insulating layer of asphalt sealed the top and held in place an iron rod suspended into the center of the copper cylinder. The rod (to the right of the cylinder) showed evidence of having been corroded with an acidic agent (see schematic below). The archaeologist Wilhelm König examined the object in 1938, and concluded that the clay pot was nothing less than an ancient *electric battery*. In the 1940's, reproductions of the "Baghdad Battery" were made at the General Electric Company, and when filled with a copper sulphate solution as an electrolyte, indeed produced a small current.



The half-cell potential (E°) for the oxidation of Cu to Cu^{2+} is -0.345 V ; for Fe to Fe^{2+} , it's $+0.447 \text{ V}$. Given that the more positive the half-cell potential, the more spontaneous the reaction, what metal is oxidized in the "Baghdad Battery"? Which metal serves as the anode? The cathode? Write the half reactions that correspond to the anode and cathode processes, and combine them into a balanced redox equation.

The Fe to Fe^{2+} couple is more positive, and hence is the spontaneous reaction. Iron (the oxidized metal) serves as the anode, and the copper electrode is the cathode.

Anode: $\text{Fe}(s) \rightarrow \text{Fe}^{2+} + 2e^-$; Cathode: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}(s)$; Net: $(\text{Fe}(s) + \text{Cu}^{2+}) \rightarrow \text{Fe}^{2+} + \text{Cu}(s)$

5. Write a short-hand notation for the cell, with the anode on the left. $\text{Fe}(s) | \text{Fe}^{2+} || \text{Cu}^{2+} | \text{Cu}(s)$

6. If the "Baghdad Battery" was a battery (and this point is still disputed), what was it used for? In the 1970's, the Egyptologist Arne Eggebrecht built a replica of the Baghdad battery and filled it with a 5% vinegar solution, as he speculated the ancients might have done. The replica generated 0.5 V with a current of 0.15 milliamperes. He then used current from the battery in a 2.5 hr experiment to electroplate a silver statuette with gold. Eggebrecht argued that the Baghdad battery could have been used for just such electroplating in ancient times. What was the total charge (Q) in coulombs that passed through the circuit?

$$Q = I \times t = 0.15 \times 10^{-3} \text{ C/sec} \times 2.5 \text{ h} \times 60 \text{ min/1 h} \times 60 \text{ s/1 min} = 1.35 \text{ C}$$

7. How much gold would have been deposited in the 2.5 hours?

$$n_e = 1.35 \text{ C} \times 1 \text{ mol } e^- / 96,485 = 1.40 \times 10^{-5} \text{ mol } e^-;$$

$$m_{\text{Au}} = 1.40 \times 10^{-5} \text{ mol } e^- \times (1 \text{ mol Au} / 1 \text{ mol } e^-) \times (196.97 \text{ g Au} / 1 \text{ mol}) = 2.8 \times 10^{-3} \text{ g Au}$$

(A major difficulty with Eggebrecht's theory is that the gold cyanide solution he used was unknown to the ancients. Many archeologists remain unconvinced that possible substitutes (e.g., gold sulphite) were available.)