

Problem of the Week (ANSWERS)

17–21 February, 2003

Oral Electrochemistry

Cavities in teeth have been filled since earliest times with a variety of materials, including stone chips, turpentine resin, gum, and metals. French dentists were the first to mix mercury with various other metals and plug the mixture into cavities. Originally developed in the early 1800s, such *dental amalgams* were gradually modified during the 19th and 20th centuries.



1. One hundred years ago, your teeth might have been filled with a copper amalgam, which contained approx. 30% copper and 70% mercury. The amalgam wasn't particularly stable over time, and could produce green-stained teeth. The staining arose from Cu^{2+} ions, generated by oxidation of the copper ($\mathcal{E}^{\circ}_{\text{red}} = 0.34 \text{ V}$). The accompanying reduction reaction is $\text{O}_2 \rightarrow \text{H}_2\text{O}$ ($\mathcal{E}^{\circ}_{\text{red}} = 1.23 \text{ V}$). To see why there was a problem with this amalgam, first balance the oxidation and reduction reactions in acid solution.

a) oxidation: (unbalanced) $\text{Cu} \rightarrow \text{Cu}^{2+}$; (balanced) $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^{-}$

b) reduction: (unbalanced) $\text{O}_2 \rightarrow \text{H}_2\text{O}$; (balanced) $4e^{-} + 4 \text{H}^{+} + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

2. Combine the two half-reactions, find the net emf, and show why corrosion of the copper occurred.

$2\text{Cu} + 4\text{H}^{+} + \text{O}_2 \rightarrow 2\text{Cu}^{2+} + 2\text{H}_2\text{O}$ (eq a must be multiplied by 2 before adding)

Emf for the oxidation of copper is -0.34 V (the sign must be reversed; the emf is not multiplied by 2); addition to the reduction potential of O_2 ($+1.23 \text{ V}$) gives $+0.89 \text{ V}$. A positive potential implies a negative ΔG ($\Delta G^{\circ} = -n\mathcal{F}\mathcal{E}^{\circ}$), and hence a spontaneous reaction.

3. A common dental amalgam mixture used today contains silver and tin along with the mercury. Such an amalgam actually consists of three solid phases having stoichiometries corresponding to Ag_2Hg_3 , Ag_3Sn , and Sn_8Hg . The standard reduction potentials for the phases are $\text{Hg}_2^{2+}/\text{Ag}_2\text{Hg}_3$, $+0.85 \text{ V}$; $\text{Sn}^{2+}/\text{Ag}_3\text{Sn}$, -0.05 V ; and $\text{Sn}^{2+}/\text{Sn}_8\text{Hg}$, -0.13 V . In conjunction with the $\text{O}_2 \rightarrow \text{H}_2\text{O}$ reaction noted above, which of these phases is the most likely to corrode? What ions will be released?

Corrosion will involve oxidation, and of the three phases, the Sn_8Hg phase has the most positive oxidation potential ($+0.13 \text{ V}$), and will be the first to corrode. Sn^{2+} ions will be released (a metallic taste could be noted in the mouth). (Note: the Ag_2Hg_3 phase is resistant to oxidation, so it might be asked why tin is used at all. A pure Ag/Hg amalgam will expand on hardening, and if packed into a tooth, would lead to cracking. A Sn/Hg mixture will contract on hardening, and a mixture of the three metals leads to an amalgam whose volume before and after setting is essentially constant.)

4. Although concentrations in the mouth are far from normal (no 1 M solutions!), compare the relative extent of oxidation of copper and silver tin amalgams by calculation of their respective K . Assume the mouth is at normal body temperature ($37 \text{ }^{\circ}\text{C}$). ($\mathcal{F} = 96,500 \text{ J/V}\cdot\text{mol}$; $R = 8.3143 \text{ J/K}\cdot\text{mol}$)

$\ln K = n\mathcal{F}\mathcal{E}^{\circ}/RT$; for the copper amalgam, $\mathcal{E}^{\circ} = +0.89$, and $\ln K = n\mathcal{F}\mathcal{E}^{\circ}/RT = 4(96,500)(0.89)/(8.3143)(37 + 273 \text{ K}) = 133$. Hence $K = 5.7 \times 10^{57}$

$\ln K = n\mathcal{F}\mathcal{E}^{\circ}/RT$; for the silver amalgam (Sn_8Hg phase), $\mathcal{E}^{\circ} = 1.23 + 0.13 = 1.36 \text{ V}$, and $\ln K = n\mathcal{F}\mathcal{E}^{\circ}/RT = 4(96,500)(1.36)/(8.3143)(37 + 273 \text{ K}) = 204$. Hence $K = 3.9 \times 10^{88}$

(Even though there is a $\sim 10^{30}$ larger equilibrium constant for the corrosion of the Ag/Hg amalgam, the copper amalgams were much more easily corroded because of their greater porosity and mechanical weakness, which allowed greater contact with body fluids.)

5. Another consequence of amalgam electrochemistry can be experienced by someone who accidentally bites a piece of aluminum foil ($\mathcal{E}_{\text{red}}^{\circ} = -1.66 \text{ V}$) (such as that used for wrapping candies) in such a way that the foil presses against a dental filling. An electrochemical cell has been created in the mouth, and a momentary sharp pain is the consequence. What serves as the anode in this "cell"? What is the cathode? The electrolyte?

Aluminum has the most positive oxidation potential ($E_{\text{ox}}^{\circ} = +1.66 \text{ V}$) and serves as the anode, the amalgam filling as the cathode, and saliva as the electrolyte. (Contact between the aluminum foil and the filling short-circuits the cell, causing a weak current to flow between the electrodes. The current stimulates the sensitive nerve of the tooth, causing an unpleasant sensation.)

6. Small pieces of gold leaf are sometimes used to decorate fancy chocolate desserts. Why does biting on such a piece of metal not cause the pain that a piece of aluminum foil does? (Hint: $\mathcal{E}_{\text{red}}^{\circ} \text{ Au}^{+} = 1.69 \text{ V}$)

The oxidation potential for Au to Au⁺ is sufficiently low (-1.69 V) that even when combined with the reduction of O₂, the resulting potential is still negative (-0.46 V). Hence the oxidation is non-spontaneous.