# Redox Challenges

## Good Times for Puzzle Fanatics

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Several years ago a colleague gave me three chemical reactions that he said actually occur but could not be balanced. It did not take long for me to realize that if they are naturally occurring, they had to be balanced. It must, therefore, be possible to balance them on paper. My colleague agreed that it should be possible to balance them but that it was very difficult and that he had never done it. Being a puzzle fanatic, I took up the challenge. He was right. These reactions can be balanced on paper, and they are difficult.

The three reactions, ordered from merely difficult to incredibly challenging are given below. Are you up to the challenges?

### The Redox Balancing Challenges

$$HIO_3 + FeI_2 + HCl \rightarrow FeCl_3 + ICl + H_2O \quad (1)$$

$$CuSCN + KIO_3 + HCl \rightarrow CuSO_4 + KCl + HCN + ICl + H_2O \quad (2)$$

$$[Cr(N_2H_4CO)_6]_4\,[Cr(CN)_6]_3 + KMnO_4 + H_2SO_4 \rightarrow$$
$$K_2Cr_2O_7 + MnSO_4 + CO_2 + KNO_3 + K_2SO_4 + H_2O \quad (3)$$

### Discussion

The reaction given in eq 1, though complicated, can be balanced using the methods taught in college freshman, and often high school, chemistry courses. The primary difficulty is that there are two different species being oxidized, iron(II) and the iodide ion, which are related to each other by stoichiometry. I often use this reaction as an example when teaching the balancing of redox reactions, to point out that even complicated reactions can be balanced by the careful application of the standard method.

The reaction given in eq 2 is more complex. It involves two oxidation and two reduction half reactions, with the further complication that both oxidation half reactions and one of the reduction half reactions are linked by formula of copper(I) thiocyanate (CuSCN). One of the reduction half reactions is a reduction of carbon(IV) to carbon(II), but in ions which are covalently bonded. A potential complication for freshman chemists is that the methods for assigning oxidation numbers to covalently bonded atoms often is taught in organic rather than freshman chemistry. If the oxidation numbers of the carbon atoms are given, or can be determined by the methods presented, this reaction also can be balanced using freshman chemistry methods. I often have assigned this challenge as an extra-credit homework problem. Freshman chemists seldom can balance this reaction without some hints. When the stoichiometric relationships involved are given as hints, though, many of them have been able to balance this reaction.

Equation 3 is the specific reaction that my colleague thought was impossible to balance. It is exceedingly difficult. The chromium-containing complex is the oxidized species. It contains chromium ions in two different oxidation states, both of which are oxidized. Of the two types of carbon atoms, one is oxidized. The other is merely hydrolyzed maintaining its oxidation state. Both types of nitrogen atoms, each initially in the –3 oxidation state, are oxidized. The atoms in the urea and cyanide ligands are covalently bonded, presenting the same difficulty as mentioned for eq 2. Counting all the different types of atoms and ions oxidized, there are five separate oxidations. All are linked stoichiometrically. The total oxidation half reaction involves hundreds of ions and molecules. The reduction reaction is trivial by comparison. It is the familiar reduction of permanganate to manganese(II). When the total reaction is balanced there are nearly 6000 electrons transferred.

I occasionally have given this reaction to a freshman chemistry class as extra credit, worth up to an A grade for the entire course. I always tell the students that it is possible to balance this reaction but that it is very difficult. I explain that it goes beyond the scope of the course and that they should not be discouraged if they cannot balance it. No freshman chemistry student of mine ever has balanced this reaction with success. In fact, it took me several hours to balance it the first time, and it took another hour to check my answer.

### The Answers

The balanced chemical reactions for the Redox Challenges[2]

$$5\ HIO_3 + 4\ FeI_2 + 25\ HCl \rightarrow 4\ FeCl_3 + 13\ ICl + 15\ H_2O \quad (4)$$

$$4\ CuSCN + 7\ KIO_3 + 14\ HCl \rightarrow$$
$$4\ CuSO_4 + 7\ KCl + 4\ HCN + 7\ ICl + 5\ H_2O \quad (5)$$

$$10[[Cr(N_2H_4CO)_6]_4\,[\,Cr(CN)_6]_3] + 1176\ KMnO_4 + 1399\ H_2SO_4 \rightarrow$$
$$35\ K_2Cr_2O_7 + 1176\ MnSO_4 + 420\ CO_2$$
$$+ 660\ KNO_3 + 223\ K_2SO_4 + 1879\ H_2O \quad (6)$$

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[2]Detailed, systematic solutions for balancing these reactions may be obtained from the author.