

${}^5E(t_2)^3(e)$ , quartet states will arise from  $(t_2)^3(e)^2$  where two  $t_2$  electrons have opposed spins. These can be worked out by adding a  $t_2$  electron to the  ${}^5T_2$  state  $(t_2)^2(e)^2$  of  $d^4$ , and their IR's are, therefore,  $(T_2 \times T_2) = A_1 + E + T_1 + T_2$ . Quartets arising from  $(t_2)^3(e)^2$  constitute the excited states in the very sharp bands that appear in the d-d spectra of octahedral high-spin Mn(II) complexes. The two broader bands appearing at lower energies in these spectra are transitions to quartet states arising from  $(t_2)^4(e)$ . Their IR's can be deduced as  $T_1 + T_2$  by adding an e electron to the  ${}^3T_1$  state from  $(t_2)^4$  of  $d^4$ , and taking the DP ( $E \times T_1$ ).

Other octahedral  $d^n$  configurations can be treated in the same way: and from the similarity between the O and T character tables, it should be a straightforward matter for students and teachers to extend the treatment to tetrahedral systems, *mutatis mutandis*.

#### Literature Cited

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## On Balancing "Redox Challenges"

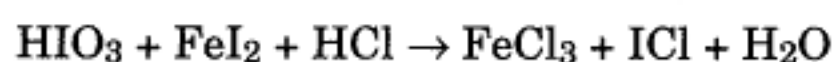
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A recent paper (1) in *this Journal* lists three redox equations which offer a challenge to the conventional techniques for balancing them. This paper offers a systematic procedure for handling such equations using nonconventional oxidation numbers and avoiding a lot of mathematics.

I tell my students in General Chemistry that *tools* like Oxidation Numbers (OxNos) are like the scaffolding used to build a cathedral: once the construction is completed, *how* it was done is irrelevant. As long as the fundamental requirement that *the sum of the OxNos is the real charge on the species*, the individual OxNos may be chosen for convenience. Stout's three equations offer beautiful examples of the benefits of going beyond the conventional. The "trick" is to put all the burden of OxNo change on just two atoms, one oxidized and one reduced, irrespective of whether it makes "chemical sense" or not.

The first reaction is:



Here we assign H, O and Cl their usual OxNos of +1, -2, and -1, respectively, and take the iodide of the iron compound "out of the game" by giving it the value it has in the product ICl, +1. Then the requirement that the OxNos sum to the charge on  $\text{FeI}_2$ , zero, gives iron the unconventional OxNo of -2.

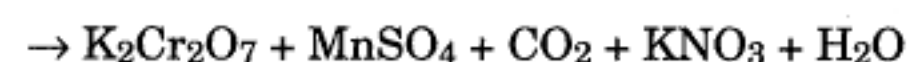
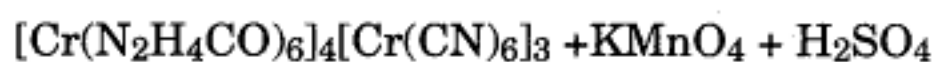
This unusual assignment results in having the iron oxidized from -2 to +3, and it is only the iodine of the  $\text{HIO}_3$  that is involved in the redox, being reduced from +5 to +1. Requiring the total increase in OxNo to be the same as the total decrease leads to the Fe of 4  $\text{FeI}_2$ 's going up in OxNo by 5 and the I of 5  $\text{HIO}_3$ 's going down by 4. This is the same stoichiometry given by Stout.

In the second equation,



we take sulfur out of the game by assigning the OxNo of the S in  $\text{CuSCN}$  to be +6, the value it has in the  $\text{CuSO}_4$  product. This requires that Cu have the OxNo of -5 (if we consider the CN group, unchanged in the redox, to be a simple group with a -1 charge). The OxNo of Cu thus goes from -5 to +2 in the  $\text{CuSO}_4$  for a change of +7 and the OxNo of the I in  $\text{KIO}_3$  goes from +5 to +1 for a change of -4. We thus take 4 of the Cu compound and 7 of the iodine compound to give Stout's stoichiometry.

The third equation given by Stout is a real challenge if the conventional OxNos for the various atoms are chosen, but is simple—if arithmetically tedious—if we let the N, H, C, and O atoms of the reactant have the same OxNos that they have in the products.



Taking the OxNo of N, O, H, and C in the reactant equal to their (conventional) values in the products, we must assign an OxNo for Cr by requiring that the sum of the OxNos in the complex compound add to zero. Thus for  $\text{Cr}_7\text{N}_{66}\text{H}_{96}\text{C}_{42}\text{O}_{24}$  we find an OxNo for Cr of  $-546/7$ , a clearly nonconventional value. The oxidation is of 7 Cr atoms going from  $-546/7$  to +6 ( $= 42/7$ ) in  $\text{K}_2\text{Cr}_2\text{O}_7$  for a total change of 7 times  $(42 + 546)/7 (= 588)$ . The reduction of Mn in  $\text{MnO}_4^-$  is from +7 to +2 in  $\text{Mn}^{2+}$ , so we need  $588/5$  Mn atoms for balance. Multiplying the Mn compound by 588 and the Cr compound by 5 gives coefficients for the equation which are half of Stout's; multiplying through by 2 to give integer coefficients gives the same equation as Stout's.

Once we get beyond their use in a single species, as with nomenclature, and involve two or more species, as with reactions, the assigning of oxidation numbers really becomes arbitrary<sup>1</sup>. They may thus be chosen to make life simpler, especially when students are taking a "second look" at OxNos. The present author admits that it may take a bit of sophistication to see beyond the "common" OxNos, but the return is an elimination of a lot of algebra irrelevant to the chemistry of the problem. As a bonus, the technique makes the pedagogically useful point that OxNos, at least for species with more than a single element, are made by chemists for chemists and are not really fundamental to nature.

#### Literature Cited

1. Stout, R.; *J. Chem. Educ.* **1995**, *72*, 1125.

<sup>1</sup>For example, in the  $\text{CN}^-$  ion, we would usually choose "chemically reasonable" OxNos of +2 and -3 for the C and the N, respectively, but -4 for C and +3 for N are also chemically reasonable. Only further information might lead us to prefer one choice over the other. I would not mark either choice incorrect.