Oxidation States versus Oxidation Numbers

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I read with interest the recent article by Hans-Peter Loock on the determination of oxidation states and strongly agree with his conclusion concerning the superiority of the Pauling method for assigning oxidation values (1). However, there are at least three points which require clarification and/or amplification.

First: I was greatly puzzled by the quoted IUPAC distinction between oxidation state and oxidation number, which implied that the latter may be applied only to the central atom of a coordination complex and is represented by a Roman numeral, whereas the former may be assigned to all of the atoms within a polyatomic species and is presumably represented, following Dr. Loock's own usage, using Arabic numerals preceded by the appropriate charge sign. As pointed out elsewhere (2), when originally introduced by the American chemist, Wendall Latimer in 1938 (3), the terms oxidation state and oxidation number were synonymous and they are still used in that sense by both my fellow inorganic chemists and by the most recent IUPAC guides to physical units (4) and to inorganic nomenclature (5). To the extent that I am able discern any semantic distinction between these two names, it would be that the term oxidation number refers to the specific numerical value assigned to the entity known as the oxidation state, much as IUPAC now uses the term charge number to refer to the numerical value assigned to the entity known as ionic charge.

It should be further noted that references 4 and 5 are also unanimous in their assertion that oxidation states/numbers are always represented using Roman numerals and never using Arabic numerals, though I am fully aware that most textbooks violate this injunction. Indeed the Freshman textbook used at Cincinnati totally inverts the conflicting IUPAC definitions which are the subject of Dr. Loock's insightful criticisms and uses the term oxidation state and Roman numerals only for the central atoms of transition metal coordination complexes, whereas the term oxidation number and Arabic numerals are used in all other contexts, such as the balancing of redox reactions, as well as in symbolizing formal charges.

Second: In light of these considerations, I would argue that what is at issue here is not a distinction between a so-called expanded versus a more restricted definition of oxidation state, but rather one of "compositional" versus "topological" oxidation states, since the origins of both the memorized IUPAC rules and the ligand removal rule are ultimately traceable to an attempt to assign oxidation values based solely on the use of a species' compositional formula, whereas the Pauling approach requires a knowledge of the species' electronic bonding topology as represented by a Lewis diagram.

Third: An overlooked area in which the difference between these two approaches is of great importance is the field of organometallic chemistry. Textbooks on this subject generally use the ligand removal rule to assign oxidation states to the central atom of an organometallic complex and, in so doing, totally ignore the role of back donation in determining the actual metal-ligand bond order (6). To take an extreme example, consider the $[Mn(CO)_4]^{3-}$ anion. Using the ligand removal rule and ignoring back donation, the Mn atom in this complex is usually assigned a compositional oxidation number of -III, thus making it a rare example of a species in which a metal atom has been forced into a negative oxidation state. However, the stretching frequency of the CO bond in its carbonyl ligands approaches that of a typical CO double bond (7), thus suggesting that the degree of back-donation is so extreme that the four MnC bonds are best represented as double, rather than as single bonds – a result which would lead instead, via the Pauling rules and the corresponding Lewis diagram, to a topological oxidation number of +V for the Mn atom – a change that is both nontrivial and conceptually significant.

Of course in most organometallic species the degree of back donation results in only a fractional change in the metal-ligand bond order and one would require the use of weighted resonance structures in order to determine the actual topological oxidation state. However, this problem, as briefly noted in several of Dr. Loock's references, also occurs in numerous organic species and affords an opportunity to forge a link between the teaching of resonance and the teaching of oxidation states.

Literature Cited

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