Oxidation Numbers

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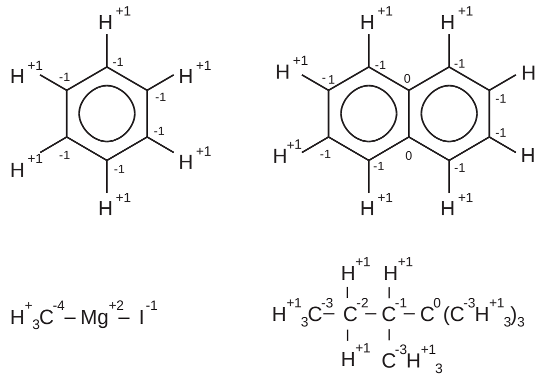
Oxidation numbers were invented by inorganic chemists. They are useful for balancing redox reactions, and coordination chemists need them for systematizing the rich world of transition metal chemistry. Organic chemists and biochemists, however, are less fond of this concept and in general use it only when dealing with "classical transition metal compounds". The problem of assigning oxidation numbers in organic chemistry, the richness of which reflects the homopolar nature of the C–C and the C–H bond, stems from the fact that it is not easy to accept that, for example, C_2H_6 does not contain carbon in essentially the same way as CH_4—a problem recognized by Chr. K. Jørgensen 30 years ago. He explains it in *Oxidation Numbers and Oxidation States* where different aspects of oxidation numbers are discussed (*1*). The numbers have been disputed by several authors (see, e.g., refs *2*–*5*), and basic chemistry textbooks give clear rules for assigning them (*6*–*9*). However, authors are usually careful not to give too many organic examples. This stems from similar problems as those already stated by Chr. K. Jørgensen. I suggest a simple modification of the rules, which eliminates this and makes it easier for students to learn and to fruitfully use the concept of oxidation numbers.

An oxidation number is assigned by applying a set of as few rules as possible, which should be simple and clear and lead to unambiguous and chemically reasonable results, if possible. The rules given in Table 1 are generally accepted. They must be applied in the order given, and we must stop as soon as the oxidation number has been obtained. Oxidation numbers obtained by applying these rules to inorganic compounds fulfill the criteria stated above. When it comes to organic molecules, however, this is not the case, as shown in Scheme I. Other examples illustrating this are catenation, dehydration, and oxidation, starting from CH_4.



Scheme I
Oxidation numbers of selected organic compounds assigned according to the rules in Table 1

What worries me is that:

1. Catenation appears as a redox reaction.
2. The oxidation number of the carbon atoms in hydrocarbons differs by 5 units, from –4 in CH_4 to zero in $C(CH_3)_4$. Scheme I demonstrates that the oxidation number of the carbon atoms of a saturated hydrocarbon molecule can vary by four units, from –3 to zero.
3. The oxidation number of the carbon atom when going from CH_4 to CO_2 changes by 8 units.
4. The oxidation number of the involved carbon atom is –2 in methanol, –1 in all other primary alcohols, 0 in a secondary alcohol, and +1 in a tertiary alcohol.
5. Hydration and dehydration of hydrocarbons appear as redox reactions in the same sense as the formation of an alcohol or an aldehyde.
6. The oxidation number of the hydrogen atom bound to an oxygen is the same as of that bound to a carbon atom.

Table 1. Rules for Assigning Oxidation Numbers (*6*)

No.	Rule / Application	Oxidation Number
1	The sum of the oxidation numbers of all atoms in the species is equal to its total charge	
2	For atoms in the elemental form	0
3	For elements of group I For elements of group II For elements of group III (except B) For elements of group IV (except C, Si)	+1 +2 +3 for M^{3+} +1 for M^{+} +4 for M^{4+} +2 for M^{2+}
4	For hydrogen	+1 in combination with nonmetals –1 in combination with metals
5	For fluorine For Cl, Br, I	–1 in all compounds –1 unless combined with oxygen
6	For oxygen	–2 unless combined with F –1 in peroxides ($O_2{}^{2-}$) –1/2 in superoxides ($O_2{}^{-}$) –1/3 in ozonides ($O_3{}^{-}$)

Table 2. Jørgensen's Axioms (*1*)

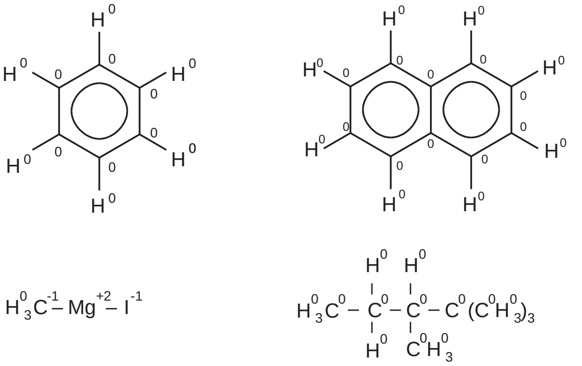
No.	Statement of Axiom	Comment
1	The sum of the oxidation numbers of the atoms in a monoatomic or polyatomic entity is the electric charge of the entity in protonic units.	–
2	If there is no serious reason to do otherwise, identical oxidation numbers are ascribed to atoms of the same element in a given compound.	Chemical evidence can constitute "serious reasons"; examples are $[S^{-2}S^{+6}O^{-2}{}_3]^{2-}$ and $\{Ga^{+1}[Ga^{+3}Cl^{-1}{}_4]\}$.
3	Oxidation numbers can be ascribed by analogy (substitution of similar atoms or groups) to compounds where the oxidation numbers are determined from the specific rules.	–
4	Reactions of an entity with the characteristic acid or base of a solvent (hydrated H_3O^+ and OH^- in aqueous solution) do not modify the oxidation numbers of the individual atoms.	One cannot maintain this axiom in an absolute sense. A clear counterexample is the reaction $Cl_2 + 2OH^- = ClO^- + H_2O + Cl^-$. Other counterexamples, if the modified rule 4 is accepted, are the saline carbides that contain $C_2{}^{-2}$ or C^{4-} as anions, which produce ethyne or methane, respectively, and the corresponding hydroxides in water, e.g., $Al_4C_3(s) + 12H_2O(l) \rightarrow 4Al(OH)_3(s) + 3CH_4(g)$.

This is chemically not reasonable! We cannot say that it is wrong, because correct balancing of redox equations is possible provided the rules are applied in a strict sense. But it violates a condition stated by Jørgensen as axiom 2 (Table 2). There is no serious reason for assigning oxidation numbers to the carbon atoms of a saturated hydrocarbon molecule in the range of −3 to zero, but there are good reasons *not* to do so. This is an uncomfortable situation, which I suggest should be changed—but without losing the very useful features of oxidation numbers and without making the rules complicated. The solution to this problem is astonishingly simple if we accept that the carbon group is so important that its nonmetals should be treated separately. Then rule number 4 should be stated as follows:

4	For hydrogen	*0 in combination with C, Si, Ge, and also B*
		+1 in combination with nonmetals
		−1 in combination with metals

It is not necessary to include the other group IV elements, because Sn and Pb are metals.

Applying the modified rule 4 to the examples in Scheme I, we observe in Scheme II that the problems have vanished. We also observe that axiom 2 is automatically fulfilled. The same is true for catenation, dehydration, and oxidation starting from methane and also for catenated silicon compounds. The modified rule 4 does not solve all problems encountered in assigning oxidation numbers, many of which can easily be handled by an experienced chemist. However, it makes this concept more useful and also easier to learn for students.



Scheme II
Oxidation number of selected organic compounds assigned according to the modified rule 4

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