

Unusual oxidation numbers in some radicalic molecules

Números de oxidación inusuales en las moléculas radicálicas

CLAUDIO GIOMINI¹, GIANCARLO MARROSU¹, LIBERATO CARDELLINI²

¹ICMMPM Dept., Via del Castro Laurenziano, 7 – 00161 Roma, Italy

²Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona, Italy

Claudio.Giomini@uniroma1.it, Giancarlo.Marrosu@uniroma1.it, l.cardellini@univpm.it

Abstract

It is generally agreed that a non-integer oxidation number may not be given to an element, unless it is present with more than one atom per molecule (or formula unit) in a given substance. Yet, the examples discussed in this paper, concerning some non-metallic oxide radicals, seem to provide exceptions to the above statement and there are further bits of evidence that some assumptions in the oxidation number theory may be objectionable. Some didactic implications are also discussed. The assignment of oxidation numbers cannot be a mere numerical exercise, but contact must be maintained with chemical reality.

Key words: oxidation number; radicals; non-metallic oxides; mental models.

Resumen

Se sabe que un número de oxidación no entero, no se puede atribuir a un elemento sin que esté presente con mas de un átomo por molécula (o por fórmula unitaria) en una sustancia. Sin embargo, los ejemplos analizados en este trabajo, concernientes a algunos óxidos no metálicos radicálicos, demuestran aparentemente excepciones a lo antes afirmado, evidenciando además que alguna de las asunciones de la teoría del número de oxidación pueda ser opinable. En el trabajo se analizan también unas implicaciones didácticas. La atribución del número de oxidación no tiene que ser una pura tarea numérica, pero tal número tiene que relacionarse con la realidad química.

Palabras clave: número de oxidación, radicales, óxidos no metálicos, modelos mentales.

INTRODUCTION

Chemistry is perceived as a difficult topic by our students, who quite often regard courses in general chemistry as unusually challenging. No matter how skilled the teacher, students develop misconceptions, as reported in the literature (TABER, 1996). In education, there is unanimous agreement with David Ausubel's statement: "The most important single factor influencing learning is what the learner already knows. Ascertain this and teach him accordingly" (NOVAK & GOWIN, 1984).

Nevertheless, there are topics, such as those related to the world of microchemistry that can only be understood in terms of a series of progressive transitions between abstract mental models of varying complexity and explanatory power (NIAZ, 1993). Maybe for this reason also, the concept of oxidation numbers is seen by our students (and some teachers too) as a bit artificial, a numerical exercise. In a study carried out on Hungarian high school students, it was found that only a minority of them balance redox equations by using oxidation numbers (TÓTH, 2001).

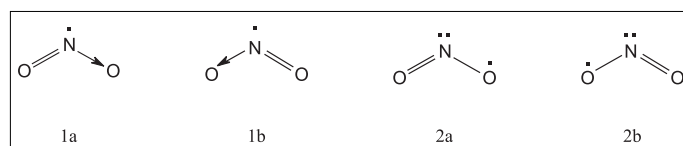
Yet, Woolf rightly warns that the oxidation number "is a useful teaching device provided that it is not treated as a purely numerical exercise, but, rather, that contact is maintained with chemical reality". (WOOLF, 1988), and we agree with him about this point.

UNUSUAL OXIDATION NUMBERS

There is not a general consensus about the definition of oxidation-reduction; yet we agree that "the only logically consistent definition of oxidation-reduction is one in which the concept is defined in terms of the change of oxidation states. The oxidation states are defined in terms of rules which are recognised as largely arbitrary". (SISLER & VANDERWERF, 1980). One of these rules states that the electrons shared between two mutually bonded atoms must be considered as totally (and not partially) gained by the more, and totally lost by the less, electronegative atom. In other words, although it is well known that charge separation along polar covalent bonds is partial, the oxidation number theory assumes it is complete and regards all the bonds between atoms of unlike elements as totally ionic. Therefore, oxidation numbers are usually integers, and it is generally agreed that a non-integer oxidation number may be given to an element only if two or more atoms are present per molecule (or formula unit) in a

given substance. So, for instance, the oxidation number of carbon in methylpropane (isobutane) turns out to be -2.5, a value that averages a -3 for each of the three primary carbon atoms with a -1 for the only tertiary one. Other examples, not taken from organic chemistry, might be the +2.5 for sulfur in tetrathionate ion, or the -1/3 for nitrogen in hydrogen azide.

Nitrogen dioxide, NO₂, seems to provide an exception to the above statement. Actually, it's a triatomic angular molecule that can be represented as a resonance hybrid between two pairs of canonical structures (fig. 1), where the unpaired electron can be "placed" on either the nitrogen, or the oxygen, atoms. The central atom can be thought of as an *sp*² hybrid (LAGOWSKI, 1973).



If the odd electron is thought of as placed on the nitrogen atom, nitrogen takes the oxidation number, +4, while both the double-bonded and the dative-bonded oxygen atoms take -2, as usual. But if the odd electron is considered to belong to one of the oxygen atoms, nitrogen takes +3, and the oxygen atoms -1.5, as an average of -2 for the double-bonded, and -1 for the single-bonded, oxygens.

Therefore, the correct oxidation numbers in NO₂ seem to be halfway between +4 and +3 for nitrogen, and between -2 and -1.5 for oxygen, depending on the weight of the two kinds of canonical structures in the real molecule.

Similar considerations apply for the dioxide radicals, ClO₂ and BrO₂, as well.

DISCUSSION

As regards the elements in NO₂, their oxidation numbers should probably be thought of as much closer to +4 and -2, respectively, owing to the fact that in N₂O₄, the dimer form of NO₂, is not peroxide. Also the bond angle value (ca. 134°) (BIRD, 1956) seems more in accordance with having the odd electron on the nitrogen. Actually, a single pair on the nitrogen would have caused an angle narrower than 120°, which is the canonical angle for a perfect *sp*² hybridization, whereas, if only one electron is present in the non-bonding *sp*² orbital, the repulsion between the σ bonding electron pairs would be greater than the repulsion between a σ pair and the odd electron. Furthermore, if NO₂ is thought of as having originated by removing an electron from the nitrite ion NO₂⁻, where all the electrons are paired, then it is more likely that the electron would be withdrawn from the less electronegative atom, i.e., nitrogen.

Yet, formal charge considerations would lead to giving a not insignificant weight to the structures where the odd electron is placed on either oxygen (OXToby, 2003). In addition, the relatively low reactivity of the radical NO₂ molecule, as well as data from esr measurements (ATKINS, KEEN, *et al.*, 1962; ATKINS & SYMONS, 1962; ZELDES & LIVINGSTON, 1961), seem to support the opinion that the contribution of either kind of structure should be quite negligible (LAGOWSKI, 1973; HUHEEY, 1972).

As for ClO₂, it is stable towards dimerization: its reluctance to dimerize probably stems from the localizing of the unpaired electron on both the chlorine and oxygen atoms (DOWNS & ADAMS, 1973). In addition, esr measurements indicate a not negligible spin density on the oxygen (ATKINS, BRIVATI, *et al.*, 1962).

CONCLUSIONS AND IMPLICATIONS FOR TEACHING

The oxidation number is essentially a "bookkeeping" concept useful in balancing the equations describing redox reactions. From this standpoint, should a substance such as NO₂ take part in a redox reaction, what is really important is that the sum of the oxidation numbers of all the atoms belong-

ing to the molecule is zero, regardless of their actual values. It is unrealistic to expect students at an early stage to deduce the arrangement of atoms just from condensed formulae. Many students not only find it difficult to maintain contact with chemical reality, but even to write Lewis structures (BRADY, *et al.*, 1990).

For a minority of high-level students who might be interested in this topic, the examples discussed in this paper could provide a further bit of evidence that, although the oxidation number is a useful tool, its assignment system relies on a given number of axioms and (somewhat arbitrary) rules, which in some cases may show inconsistencies. In particular, one of these axioms states that, when atoms share electrons and covalent bonds are formed, the above assignments are made "on the basis of some perfect or approximate separation of an *integral* number of electrons" (JØRGENSEN, 1969). It follows that "nonintegral oxidation numbers may usually be explained as being averages of reasonable assignments of oxidation numbers to individual atoms" (SWINEHART, 1952), where "reasonable" probably means, or refers to, integral values (and word "usually", not clarified by the author in the further course of his article, possibly leaves the door not completely closed to possibilities such as those we pointed out in the present paper).

We show here that, if a molecule has to be described by means of several resonant structures, such that the different "locations" of the electrons may produce different oxidation numbers for the same atom, this atom might have to be given a non-integer oxidation number, even if it is the only atom of that element present in the molecule.

This result is in contradiction with the above quoted statements of Jørgensen and Swinehart (for the latter author, at least partly), and points out that some of the rules concerning oxidation number assignments may be objectionable.

In summary, this paper does not recommend changing the set of rules, which is largely self-consistent. It just wants to make teachers more aware of both the rules' limitations and the criticism that some of them might receive from people who are more deeply concerned with the subject. It would also warn teachers about the problems that could arise if molecules such as those dealt with in the paper were chosen to illustrate the subject of oxidation numbers in the classroom. Obviously, these problems and the discussion that they could stimulate would be welcome in a class of students who are proficient in the subject.

BIBLIOGRAPHY

- ATKINS, P.W.; BRIVATI, J.A.; KEEN, N.; SYMONS, M.C.R. & TREVALION, P.A. (1962). Oxides and Oxy-ions of the Non-metals. Part III. Oxy-radicals of chlorine. *Journal of the Chemical Society*, 4785-4793.
- ATKINS, P.W.; KEEN, N. & SYMONS, M.C.R. (1962). Oxides and Oxyions of the Non-metals. Part II. CO₂- and NO₂. *Journal of the Chemical Society*, 2873-2880.
- ATKINS, P.W. & SYMONS, M.C.R. (1962). Oxides and Oxy-ions of the Non-metals. Part IV. Nitrogen Derivatives. *Journal of the Chemical Society*, 4794-4797.
- BIRD, G.R. (1956). Microwave Spectrum of NO₂: a Rigid Rotor analysis. *The Journal of Chemical Physics*, **25** (5), 1040-1043.
- BRADY, J.A., MILBURY-STEEN, J.N. & BURMEISTER, J.L. (1990). Lewis Structure Skills: Taxonomy and Difficulty Levels. *Journal of Chemical Education*, **67** (6), 491-493.
- DOWNS, A.J. & ADAMS, C.J. Chlorine, Bromine, Iodine and Astatine: in *Comprehensive Inorganic Chemistry*, vol. 2., A.F. TROTMAN-DICKENSON *et al.* (eds.), Pergamon Press: Oxford, UK, 1973, chap. 26, 1369.
- HUHEEY, J.E. (1972). *Inorganic Chemistry*, Harper & Row: New York, USA, 127 (footnote).
- JØRGENSEN, C.K. (1969). *Oxidation numbers and oxidation states*, Springer-Verlag: Berlin.
- LAGOWSKI, J.J. (1973). *Modern Inorganic Chemistry*, Marcel Dekker: New York, USA, 399.
- NIJAZ, M. (1993). "Progressive Problemshifts" Between Different Research Programs in Science Education: A Lakatosian Perspective. *Journal of Research in Science Teaching*, **30** (7), 757-765.
- NOVAK, J.D. & GOWIN, D.B. (1984). *Learning how to learn*, Cambridge University Press: Cambridge, NY, 40.
- OXTOPY, D.W.; FREEMAN, W. A. & BLOCK, T.F. (2003). *Chemistry: Science of Change (4th Edition)*, Brooks/Cole-Thomson Learning: Stamford, CT, USA, 140.
- SISLER, H.H. & VANDERWERF, C.A. (1980). Oxidation-reduction. An example of chemical sophistry. *Journal of Chemical Education*, **57** (1), 42-44, 44.
- SWINEHART, D.F. (1952). More on Oxidation numbers. *Journal of Chemical Education*, **29** (6), 284-285.
- TABER, K.S. (1996). Chlorine is an oxide, heat causes molecules to melt, and sodium reacts badly in chlorine: a survey of the background knowledge of one A-level chemistry class. *School Science Review*, **78** (282), 39-47.
- TÓTH, Z. (2001). Students' Strategies and Misconceptions in Balancing Chemical Equations. Implications for Classroom Practice. 6th ECRICE, Aveiro: Abstracts, 59-61.
- WOOLF, A.A. (1988). Oxidation Numbers and Their Limitations. *Journal of Chemical Education*, **65** (1), 45-46, 45.
- ZELDES, H. & LIVINGSTON, R. (1961). A Paramagnetic Species in Irradiated NaNO₂. *The Journal of Chemical Physics*, **35** (2), 563-567.

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