



### Comprehensive definition of oxidation state

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## Comprehensive Definition of Oxidation State (IUPAC Provisional Recommendation)\*

Pavel Karen<sup>1,‡</sup>, Patrick McArdle<sup>2</sup>, and Josef Takats<sup>3</sup>

<sup>1</sup>*Department of Chemistry, University of Oslo, P.O.B. 1033 Blindern, 0315 Oslo, Norway;* <sup>2</sup>*School of Chemistry, NUI Galway, Galway, Ireland;* <sup>3</sup>*Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada*

*Abstract:* Oxidation state (OS) is defined using ionic approximation of bonds. Two principal algorithms are outlined for OS determination in a compound described by a Lewis formula or bond graph. Typical origins of ambiguous OS values are pointed out, and the relationship between OS and the  $d^n$  electron configuration of transition metals is commented on.

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‡ Corresponding author: E-mail: [pavel.karen@kjemi.uio.no](mailto:pavel.karen@kjemi.uio.no)

### 1 Preamble

Oxidation state (OS) is a simple attribute of an element in a compound.<sup>1</sup> As an electron count, it scales trends in redox and acid-base properties, or in physical properties such as magnetism, and is a key component when tracking the course of chemical reactions. Thus the concept of OS is important, and so is an agreed-upon definition of what OS is and the algorithmic manner in which it is to be calculated. In the absence of a true definition, algorithms have thus far been used to define OS.<sup>2</sup>

This Recommendation proposes a definition of OS based on ionic approximation of chemical bonds, illustrated on a molecular-orbital (MO) scheme and deduced from electronegativity considerations (Allen's scale). Two algorithms are formulated for the determination of OS in molecules, ions, and extended solids, and illustrated with examples. Limits beyond which OS ceases to be well defined or becomes ambiguous are exemplified; requiring additional measurements, round offs, estimates or plain postulates. Specific uses that justify a Nominal OS are also explained.

The present authors have published a comprehensive Technical Report on OS [1]. It provides a summary of previous work and discussions concerning OS, and gives numerous examples of the application and use of algorithms to determine OS.

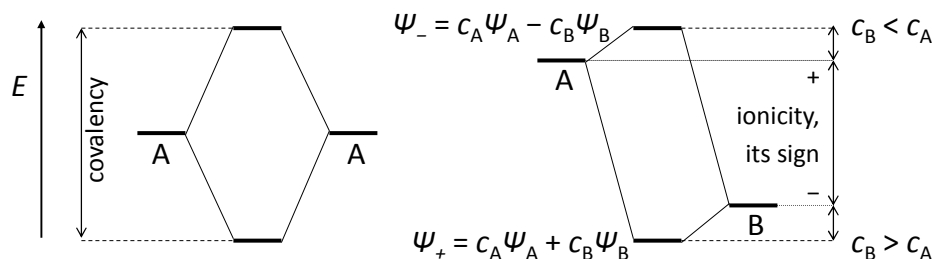
<sup>1</sup> An alternative term oxidation number is also used in English, referring to the numerical value rather than the atom's state.

<sup>2</sup> In addition, a rule-based approach of postulated OS values for relevant elements remains useful at the elementary teaching level, prior to bonding considerations. Such sets of rules of pedagogically suitable complexity can be found in numerous textbooks of chemistry.

## 2 Definition

A recommendation has a normative side that suggests what should be done and a practical side that reflects the common use. Here the normative side is expressed in the generic definition: *OS is the atom's charge after ionic approximation of its bonds.*

The *atom's charge* is the usual valence-electron count relative to the free atom, since OS is a quantitative concept that operates on counted electrons. Several criteria may be considered for the sign of the *ionic approximation* [1], but only one of them is reflective of the current use and common values of OS; the atom's contribution to the bonding MO, which is associated with the atomic-orbital energy as illustrated in Fig. 1.



**Fig. 1** The essence of ionic approximation based on contribution to the bonding MO. The mixing coefficients  $c_A$  and  $c_B$  refer to the atomic-orbital wavefunctions  $\psi_A$  and  $\psi_B$  in an LCAO-MO approach.

Fig. 1 implies that while AA bonds are divided equally, the ionic approximation of AB assigns the bond's electrons to the atom that contributes more to the bonding MO. The said contribution therefore does not concern the electrons' origin upon bond formation, only their final allegiance [1a].

Then on the practical side: In an AA bond, the two atoms are not always equivalent as Fig. 1 may imply. For example, if the NN bond in  $N_2O$  were extrapolated ionic, the central-nitrogen would have charge<sup>3</sup> of +5 and the terminal one -3. Thus the generic definition needs to be narrowed to reflect the normal or common use of the term OS:

### **OS is the atom's charge after ionic approximation of its heteronuclear bonds**

In this general definition, bonds between atoms of the same element are not replaced by ionic ones even if the two partners have a different contribution to the bonding MO(s); they are always divided equally.

<sup>3</sup> As a physical variable, the charge of an atom (even if hypothetical) is a number with sign preceding its value in units of elementary charge. As a nomenclature symbol in chemical formulas and names, ionic charge comes with trailing sign. Similarly, OS as a nomenclature symbol is in roman numerals.

### 3 Ionic approximation from electronegativity

In common use, the sign of the ionic approximation is obtained from electronegativities rather than MO schemes.<sup>4</sup> Of several scales discussed in Appendix B of ref. 1, only the Allen electronegativity (Section 6.1) is truly independent of OS since it relates to the average valence-electron energy of the *free* atom [2,3,4]; as if the bonds implied in Fig. 1 were abstracted away, Fig. 2. The ionic approximation then assigns the bond electrons to the more electronegative partner.<sup>5</sup>

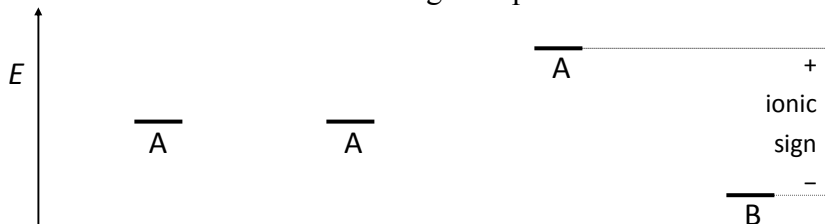


Fig. 2 Ionic-approximation sign according to relative energies of the free-atom valence orbitals, conveniently derived from Allen's electronegativities.

The ionic approximation by electronegativity has a caveat due to the electron allegiance introduced in Section 2: When the more electronegative atom is bonded as a Lewis acid (a so called Z-type ligand, ref. 5), its acceptor orbital is at high energy. Under ionic approximation, the less-electronegative Lewis-base donor, typically a late transition metal, is therefore assigned the electrons it supplied to form the adduct bond. As pointed out in ref. 6, such an electron allegiance can reveal itself via the adduct formation being reversible.

## 4 Algorithms

There are two closely related general algorithms to calculate OS:

### 4.1 Algorithm of assigning bonds

works on Lewis formulas of molecules and ions which show all valence electrons (Fig. 3). Its practical formulation uses electronegativity to deduce the ionic sign:

**OS equals the atom's charge after its homonuclear bonds have been divided equally and heteronuclear bonds assigned to the bond partners according to Allen electronegativity, except when the electronegative atom is bonded reversibly as a Lewis-acid ligand, in which case it does not obtain that bond's electrons.**

<sup>4</sup> MO schemes soon become complicated, making the ionic-sign allocation by orbital contributions or energies difficult and by atomic gross-population charges somewhat method dependent.

<sup>5</sup> Needless to say, the ionic approximation by the A–B electronegativities is a simplification. When they are close (such as for H–P, H–Te or C–Se), the ionic signs are better guided by analogies (see Section 5.4).

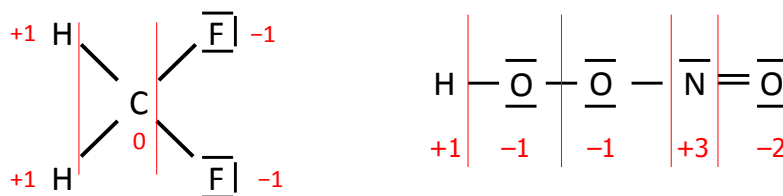


Fig. 3 OS (in red) in  $\text{CH}_2\text{F}_2$  (left) and in peroxyntrous acid (right), via assigning bonds to more electronegative partners on Lewis formula with all valence-electron pairs drawn as dashes.

The bond order of the homonuclear bonds to be divided may influence OS. It will do so when the segment of all the  $-\text{AA}-$  pair bonds, with their ionic-approximation signs, is not symmetrical. Thus, while the  $\text{OO}$  bond order in Fig. 3 (right) is irrelevant because the  $-\text{OO}-$  segment has a mirror symmetry, the  $\text{NN}$  bond order in an octet-fulfilling  $\text{N}_2\text{O}$  Lewis formula controls the OS: consider  $\overline{\text{N}}=\text{N}=\overline{\text{O}}$  versus  $|\text{N}\equiv\text{N}-\overline{\text{O}}|$  [1b].

The caveat of reversibly-bonded Lewis-acidic electronegative partner (Section 3) is illustrated with the  $\text{Rh}-\text{S}$  bond in  $\text{O}_2\text{S}-\text{RhCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$  [7] in Fig. 4. The electronegative S atom, here a Lewis acid, does not keep the bond pair, the allegiance of which follows from reversibility of this adduct back into  $\overline{\text{SO}}_2$  and  $\text{RhCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}$ .

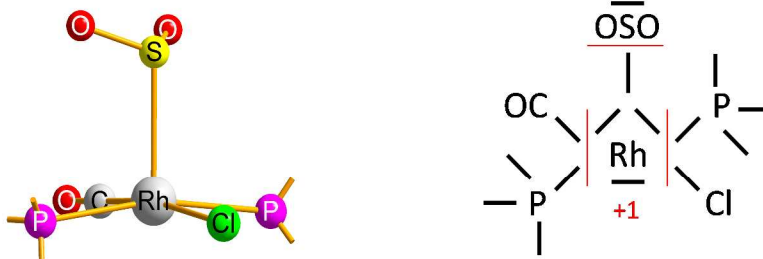


Fig. 4 OS of Rh by assigning bonds. Assignment according to electronegativity invokes the caveat of reversibly bonded  $\text{SO}_2$  as a Lewis acid, which does not keep the pair, Rh does.

## 4.2 Algorithm of summing bond orders

works on Lewis formulas and bond graphs. A bond graph represents the infinite periodic network of an extended solid [8,9]. It is constructed on a stoichiometric formula of the network's repetitive unit, with atom symbols connected with a line for each instance of atom's bonding connectivity. Each line carries its own specific bond order.

**Heteronuclear-bond orders are summed at the atom; as positive if that atom is the electropositive partner in a particular bond and negative if not, and the atom's formal charge (if any) is added to that sum, yielding OS.**

In bond graphs of extended 3D structures, there are no formal charges. The obtained "ionized bond order sum", iBOS,<sup>6</sup> then equals OS directly as illustrated in Fig. 5 on the  $\text{AuORb}_3$  perovskite [10], where OS and bond orders follow from the  $8-\text{N}$  rule at O,  $8+\text{N}$  rule at Rb, and  $12-\text{N}$  rule at Au. For glossary of these rules, see ref. 1c.

<sup>6</sup> Named in analogy to the bond-valence sum, BVS, evaluated from structure data of extended solids.

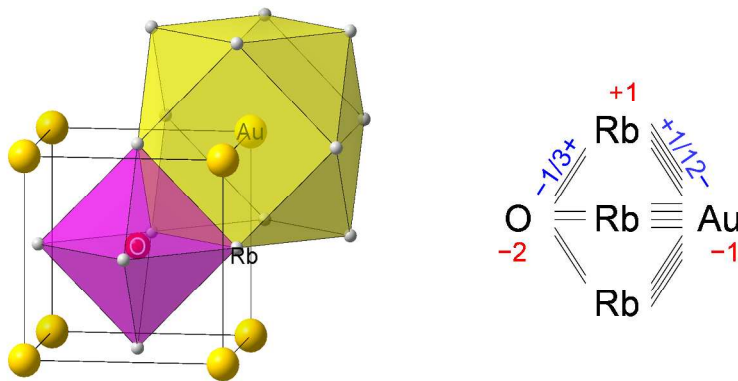


Fig. 5 Unit cell and coordination polyhedra of the AuORb<sub>3</sub> perovskite, with its bond graph of ideal bond orders (values in blue) and OS (in red).

Application to molecules is illustrated in Fig. 6. On the left, a Lewis formula with no formal charges yields  $OS = iBOS$  directly. On the right, the formal charge (FC) must be added to the sum at each atom;  $OS = iBOS + FC$ .



Fig. 6 OS (in red) by summing ionized bond orders (in blue) in Lewis formulas. Left: in CH<sub>2</sub>F<sub>2</sub> directly. Right: in CO, with nonzero formal charges (in black, with trailing sign).

Bond orders in extended solids are not always obvious and may have to be estimated from bond lengths. This is done by converting each bond length into the so-called bond valence, which is a value entirely equivalent to the bond order in terms of two-electron bonds in molecules. The origins of the bond-valence approach, one ionic [11] and one covalent [12], are associated with Linus Pauling. In ref. 12, an expression is given that has morphed into the current relation for bond valence versus bond length:

$$BV_{ij} = \exp [(R_{ij}^0 - d_{ij})/B] \quad (1)$$

where  $BV_{ij}$  and  $d_{ij}$  are the respective bond valence and distance of the atoms  $i$  and  $j$ ,  $R_{ij}^0$  is the single-bond length between them, and  $B$  is a variable parameter often fixed to 0.37. For more details, examples and relevant references, consult ref. 1.

## 5 Epilogue

Applications of OS in chemistry are wide and deal with a cornucopia of chemical compounds and materials. It is therefore not surprising that for some compounds one value does not fit all uses, or that dedicated measurements or computations are needed to ascertain the actual OS. Here we list the most important such situations; for more details and examples, see ref. 1.

## 5.1 Non-innocent ligands

Redox-active ligands, called “non-innocent” after Jørgensen [13,14], render OS less obvious when combined with a redox-prone central atom. Examples include complexes of O<sub>2</sub>, NO and dithiolenes, discussed in ref. 1. Drawing their Lewis formula requires information from diffraction and spectral data about bond orders. The OS of the transition-metal center can often be ascertained from spectral and magnetic measurements.

## 5.2 Metallic compounds

When bonding and antibonding orbitals/bands overlap in a metal, we are no longer entitled to make the ionic extrapolation implied by Fig. 1. There are simple metallic compounds of obvious OS, such as the golden TiO (+2), dark RuO<sub>2</sub> (+4), or silvery ReO<sub>3</sub> (+6), but, eventually, the assignment of conducting electrons to one of the bonded atoms has its limits. An example is the AuNCa<sub>3</sub> perovskite [15], where neglecting its metallic character suggests Au<sup>3-</sup> anions for which there is no support in theory.<sup>7</sup> Such an OS is merely a practical value for redox balancing, like setting OS = 0 for all metals in intermetallic phases of metallic character (not the semiconducting Zintl phases), or for those inner atoms in metal clusters that are solely bonded to other metal atoms.

## 5.3 Nominal OS

In systematic descriptive chemistry, OS is used to sort out compounds of an element; in electrochemistry, it represents the electrochemically relevant compound or ion in Latimer and Frost diagrams of standard (reduction) potentials. Such a purpose-oriented OS may differ from the value obtained by definition and is termed nominal, here “systematic” and “electrochemical”. Consider thiosulfate, the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> anion: The sulfur–sulfur bond is practically a single bond, which yields OS = +5 for the central S and –1 for the terminal S atom by both algorithms [1d]. The electrochemical OS of sulfur in thiosulfate is their average, +2. On the other hand, a systematic OS of +6 may be chosen for the central S atom, as if the sulfur–sulfur bond were approximated ionic, to emphasize the similarity of the peripheral O and S atoms obtaining all OS = –2. Nominal OS may also be relevant in organic chemistry where a strict concept of OS is most useful when applied to functional-group redox reactions.

## 5.4 Need for choices, estimates, and round offs

Usage-related choices define the nominal OS, vide supra. Options arise also when the AB ionicity in Fig. 1 approaches zero and the distinction between positive and negative OS wanes. In ref. 1e, this is illustrated using H<sub>3</sub>PO<sub>3</sub> where two alternative OS assignments are possible due to the almost equal electronegativities at the P–H bond. A similar example is CSe<sub>2</sub> where OS of –2 for Se is assigned via MO considerations or by analogy with CO<sub>2</sub>. The same OS suits also –C–Se–C– compounds. For intermetallics of metallic character, the ultimate choice of OS = 0 is best if needed for redox chemistry.

<sup>7</sup> Ref. 15 suggests a 6s<sup>2</sup>-stabilized Au<sup>-</sup> anion and 2e<sup>-</sup> as in an electride.



Subtler estimates or round offs are required for compounds with electrons delocalized over nonequivalent atoms, manifested by a set of weighted resonance formulas; as an example in 1*H*-pentaazole [1e], N<sub>5</sub><sup>+</sup> [1b], or thiosulfate [1d]. Round offs are needed also in compounds that enter bonding compromises, as exemplified with S<sub>4</sub>N<sub>4</sub> in ref. 16.

Rounding is also necessary for bond-valence sums after the bond-length to bond-valence conversions with eq. 1. Their decimal values stem from the statistical distribution of bonding compromises in the set of compounds used to obtain the single-bond length parameter  $R_{ij}^0$  in eq. 1.

On the other hand, reasonable fractions of small integers are obtained for OS in compounds such as B<sub>6</sub>H<sub>10</sub> or B<sub>10</sub>C<sub>2</sub>H<sub>12</sub> [1f], or when two vicinal OS are indistinguishably mixed, such as for Fe in YBaFe<sub>2</sub>O<sub>5</sub> [1g], or when the ionic charge is distributed over several equivalent atoms such as in B<sub>6</sub>H<sub>6</sub><sup>2-</sup> [1d] or I<sub>3</sub><sup>-</sup> and N<sub>3</sub><sup>-</sup> [1h]. Also OS in non-stoichiometric solids with randomly distributed defects is decimal: NiO<sub>1.031</sub> with interstitial oxygens has Ni of OS = +2.062, and so does Ni<sub>0.970</sub>O with nickel vacancies.

## 6 Addendum

### 6.1 Allen electronegativity scale

Allen electronegativities in Pauling units [2,3,4]

H 2.300							He 4.16
Li 0.912	Be 1.576	B 2.051	C 2.544	N 3.066	O 3.610	F 4.193	Ne 4.787
Na 0.912	Mg 1.293	Al 1.613	Si 1.916	P 2.253	S 2.589	Cl 2.869	Ar 3.242
K 0.734	Ca 1.034	Ga 1.756	Ge 1.994	As 2.211	Se 2.424	Br 2.685	Kr 2.966
Rb 0.706	Sr 0.963	In 1.656	Sn 1.834	Sb 1.984	Te 2.158	I 2.359	Xe 2.582
Cs 0.659	Ba 0.881	Tl 1.789	Pb 1.854	Bi 2.01	Po 2.19	At 2.39	Rn 2.60

Sc 1.19	Ti 1.38	V 1.53	Cr 1.65	Mn 1.75	Fe 1.80	Co 1.84	Ni 1.88	Cu 1.85	Zn 1.59
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Y 1.12	Zr 1.32	Nb 1.41	Mo 1.47	Tc 1.51	Ru 1.54	Rh 1.56	Pd 1.58	Ag 1.87	Cd 1.52
Lu <sup>[a]</sup> 1.09	Hf 1.16	Ta 1.34	W 1.47	Re 1.60	Os 1.65	Ir 1.68	Pt 1.72	Au 1.92	Hg 1.76

[a] Variation across the lanthanoid series has not been evaluated.

## 6.2 OS and $d^n$ configuration

The configuration  $d^n$  is a central-atom descriptor in transition-metal complexes. For a transition metal of  $N$  valence electrons,  $d^n$  yields OS as:

$$OS = N - n \quad (2)$$

A problem arises when that central atom acts as a Lewis base and donates one of its  $d^n$  non- or anti-bonding electron pairs to an acceptor ligand (Lewis acid, a Z-type ligand [5]): Whereas OS remains the same since the ionic approximation assigns the donated electron pair back to the Lewis base, the coordination geometry and magnetism at the central atom may no longer refer to the original  $d^n$  before that donation.

One of the examples discussed in ref. 1 is the Au–B bond in Fig. 7 [17], where two Au  $d$ -electrons populate the weakly bonding MO so that Mössbauer spectroscopy still sees this MO's two electrons together with the rest of  $d$  electrons on Au as  $d^{10}$ , suggesting OS = +1 for gold, in accord with the OS definition in Section 2. Yet the coordination at Au is square planar, typical of  $d^8$  Au<sup>3+</sup>. The square-planar Au appears because the donated Au  $d$ -electron pair became the Au–B bond itself, and the geometry is now controlled by the energy minimum for the remaining 8 Au  $d$  electrons in the weakly antibonding MOs. To avoid the emerging ambiguity of the  $d^{10}$  “spectroscopic” versus the  $d^8$  “ligand-field” or “magnetic” configurations, a notation used by Parkin [5] may describe the central atom: Au of  $n = 10$  in  $d^{n-2}$ , where “2” symbolizes the weakly bonding “donated”  $d$ -electron pair,  $n$  enters eq. 2 for OS determination, and  $n-2$  are the electrons in  $d$  orbitals subject to ligand field.

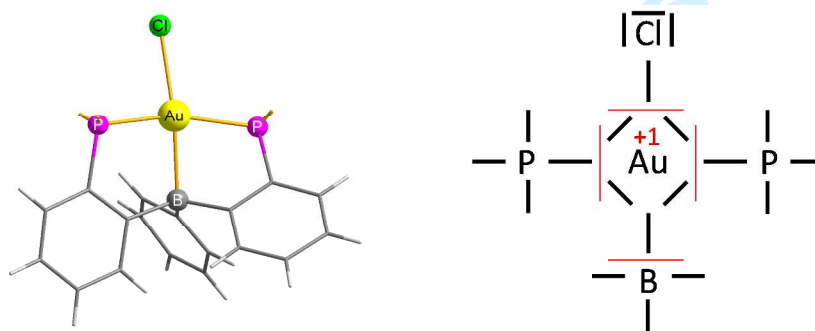


Fig. 7 Square-planar Au bonded to more electronegative B acceptor in a Z-type ligand [17].

In the same way for similar adducts of Z-type ligands and transition-metal Lewis bases: Rhodium in Fig. 4 has configuration  $d^{n-2}$  of  $n = 8$  that yields OS = +1 from eq. 2 (Rh is assigned the adduct-bond electron pair it donated) while the  $n-2 = 6$  electrons at the low-

1  
2  
3 spin 4d atom comply with the square-pyramidal coordination. More examples are in ref.  
4  
5 1.  
6

## 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

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