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Toward a definition of valence as a quantity (IUPAC Technical Report)

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Abstract: Valence has a rich history in chemistry, as a bonding concept, in terms of quantitative context, and as a true quantity. In the latter, a survey preceding this project revealed differing perceptions of valence values and helped formulate candidate definitions. This IUPAC task group evaluated nine quantities behind eight alternative definitions on 39 chemical entities of 48 bonding formulas, each giving a set of meaningful values with mutual relationships. Given the reflection principle of IUPAC normative work, 15 comparative examples with high variation of these alternative valences for an element were selected, and chemistry articles in English searched for valence-termed quantities of the compared compounds to imply the definition behind the stated valence value, the frequency of such use, and the chemistry field. Summarized preferences for the alternative definitions show two main areas of use. Organic and physical chemists count valence as a number of two-electron bonds at the atom. Inorganic chemists working with semi-metallic and metallic elements use *n*-valent as an adjective for oxidation state. The diverse yet infrequent use cannot be covered by a single definition of the valence quantity. Clarity in articles that use valence as a quantity is essential and achievable by stating the intended context.

Keywords: Bond order; bond valence; Lewis formula; valence; valence electrons.

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1 Introduction

The term valence has a long history in chemistry and has carried various and changing connotations. Referring to the atom's ability to bond, valence enters the name of many chemistry concepts, some descriptive, some more quantitative. However, as a quantity, valence does not have a single and uniquely accepted definition; it is all things to all people so to speak. That is a disadvantage; differing perceptions may obscure communication. In general, valence as a quantity describes a specific bonded atom.

The current IUPAC definition of valence in the Gold Book is from the "Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)".[1] Valence is "the maximum number of univalent atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted." No examples are given, and the meaning of "element under consideration" or "fragment" is open to interpretation. The circular wording that defines valence with "valent" is alleviated by stating H and Cl as univalent examples.

After a period of discussions, IUPAC decided to test whether a comprehensive definition of valence could be formulated. A task group was established, with members from the sponsoring IUPAC bodies listed above. In preparation for the project, an anonymized survey was conducted among members of these IUPAC groups in 2016/7, focusing on numerical valence assignments. It confirmed that chemists' perception of valence as a quantity corresponds to several simple, heuristic, alternative definitions. After a review of quantitative aspects of valence-containing terms and analysis of the valence history up to the current use, the possible definitions of valence as a quantity were tested on 39 chemical entities with several types of formulas. Respecting the IUPAC reflectivity principle meant looking for definitions that are with high consistency behind valence values used in chemistry papers. This Technical Report describes the results of these steps and provides details on the quantities behind the alternative definitions of valence, including their mutual relations. It analyzes the current use of the term valence as a chemical quantity in general and in selected telling examples in particular. This Technical Report will be followed by a formal IUPAC Recommendation on the use of the valence quantity and guide it to avoid ambiguities.

2 The history of the concept of valence

The etymology of valence in Chemistry stems from Latin words *valentia* (strength or capacity) and *valor* (worth or value). It expresses the ability of an atom to bond other atoms, the combining power of an element. The sole term "valence" (alternative spelling "valency") covers the quantitative aspect noticed early on. The outline of how the use of this term in English developed over the years follows. However, we may start several decades before the valence quantity appeared. After the introduction of quantitative chemistry by Lavoisier and Proust, electrochemistry by Davy, constant volume law by Gay-Lussac, and after Dalton's atomic theory with relative atomic mass, which all enabled the Berzelius' summarizing law of chemical proportions.[2]

Berzelius uses the chemical reaction term "oxidation" as a quantity "degree of oxidation", even in an article title "Experiments on the Nature of Azote, of Hydrogen, and of Ammonia, and upon the Degrees of Oxidation of which Azote is susceptible".[3] In Germany, Friedrich Wöhler calls the fixed ratios of oxygen to metal in manganese oxides "Oxydationsstufen" (oxidation grades) on p. 4 of his 1834 textbook Basics of Chemistry, Inorganic Chemistry[4] as well as in its 1858 twelfth edition. In 1852, Edward Frankland described in "XIX. On a new series of organic bodies containing metals"[5] p. 440 the "combining power" of an element in a compound, which is always satisfied by the same number of involved atoms. First in 1885, Frankland and Japp in the textbook "Inorganic Chemistry"[6] use the term valency for this concept when stating that "atomicity, equivalence, valency or atom-fixing power" are the terms to characterize this "combining power." What happened in the meantime?

In the German-language sphere, August Kekulé proposed in 1857 "Ueber die s. g. gepaarten Verbindungen und die Theorie der mehratomigen Radicale" or About the so-called paired connections and the Theory of polyatomic radicals[7] where carbon is "vierbasisch" or "vieratomig" so that it is equivalent to four hydrogens and its *atomicity* equals 4. Lothar Meyer in his 1864 book "Die modernen Theorien der Chemie"[8] favors on p. 67 terms "ein-, zwei-, drei-und vierwerthig"[1] (with "dreiwerthig N" already in Karl Weltzien's[2] paper "Systematic compilation of organic compounds"[9] in 1860) and states that "uni-, bi-, tri-, and quadrivalent" would be acceptable as well. In 1865, August Wilhelm von Hoffmann, in his book "Modern Chemistry, Experimental and Theoretic",[10] suggests on pages 168–9 to replace the "vague and rather barbarous expression, *atomicity*" with the term quantivalence and its adjectives monovalent, bivalent, trivalent, etc. In German, the term quantivalence quickly shortens into Valenz. In 1867, Kekulé, then already at the University of Bonn, uses Valenz once in a personal

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[1] On page 100, a single use of valence refers to Fe atom forming 4 bonds in gaseous Fe_2Cl_6 stated as "Quadrivalenz des Eisens", while a few lines above, this iron is referred to as "4werthig" (4-valued).

[2] One of three organizers (together with Kekulé and Wurtz) of the 1860 Karlsruhe Congress.

statement inside an article on mesitylene.[11] In 1868, Karl Hermann Wichelhaus, at the Humboldt University of Berlin, has Valenz even in the title of one version[12] of his article on phosphorus compounds.[3] The terms Valenz and Wertigkeit persisted, more or less as synonyms.

In 1893, Alfred Werner published his concept of complexes,[13] explained their bonding, and proved it with isomerism in the coordination octahedron of two different ligands around a central atom M. That atom's *Wertigkeit*, such as M^{III} in $[M(NH_3)_6]X_3$ or $[M(NH_3)_5X]X_2$ or $[M(NH_3)_4X_2]X$, follows from the number of bonded "einwertiger" (monovalent) "radicals" X (single-charged monoatomic ions). His *Valenz* of the above $[M(NH_3)_5X]$ "radical" (a 2+ cation) is the difference of the M "wertigkeit" and of the total of "einwertiger" X directly bonded to M, hence $3 - 1 = +2$. Coordinated molecules like NH_3 or H_2O do not count. Valenz is the plain number of "einwertiger radikaler" (monoatomic single-charged ions) that can be bonded to the atom/group/ion in question. Werner therefore points out on p. 328 of "Beitrag zur Konstitution anorganischer Verbindungen" (Contribution to the constitution of inorganic compounds)[13] that we must distinguish between the valence number (Valenzzahl) and the coordination number. The latter is the count of atoms or groups directly bonded to a central atom. 16 years later, in the revised and expanded 2nd edition of his inorganic chemistry textbook (Newer views in the field of inorganic chemistry)[14] about the constitution of inorganic compounds, Werner introduces two terms that are still in use besides the coordination number; *Hauptvalenz* and *Nebenvalenz*, translated as primary and secondary valence in the IUPAC Red Book 2005 Recommendations[15] p. 144. Werner's measure of primary valence is the number of strictly monovalent atoms (like hydrogen) that the atom in question would bond, denoted as its valence number on p. 18 and 62 of his book[14]. That atom's secondary valence, p. 50 and 62, bonds molecules able to exist on their own. The coordination number introduced on p. 52 is the number of atoms directly bonded to the central atom regardless whether by primary or secondary valency.[4]

In the first decade of the 20th century, it was realized that the English expression *valence number* and likewise German terms *Valenz* or *Wertigkeit* need to adopt both positive and negative values in order to simplify teaching redox reactions. This was pointed out by Richard Abegg for "valenz" in 1904[16] (p. 344). In his 1909 edition of "Handbuch der Anorganischen Chemie" Vol. III., Part 2,[17] Abegg uses positive and negative "valenz" (p. 33), whereas the more frequent "wertigkeit" appears solely as a positive number (p. 455), even when it refers to anionic charges on p. 167. In the period 1909–1915, Nelson et al. published a series of papers on "The Electron Conception of Valence." In the fourth paper,[18] they state: "The valence of an element may be defined as the number of corpuscles (negative electrons) of an atom of that element loses or gains to form chemical bonds." They also assumed that every chemical bond formed between two atoms involves transfer of such a corpuscle from one atom to another.

In 1913, William Bray and George Branch suggested in a paper "Valence and Tautomerism"[19] splitting the term *valence number* into two quantities: *polar number* and (total) *valence number*, the former according to usage in inorganic chemistry and the latter in organic chemistry. For example, N in NH_4Cl would then be assigned −3 by inorganic chemists and 5 by organic chemists. In the same paper, a footnote states that the "polar number" is synonymous with the German *Wertigkeit*. The same year, Böttger in the 3rd edition of his book on qualitative analysis[20] on pages 97–101 illustrates that *wertigkeit* of ions is a plain number of positive or negative ionic charges, while stating that for elements (atoms) the prevailing view is that *wertigkeit* is given by positive or negative integers. Two numerical examples follow later on, −1 in chloride and −3 of N in ammonium cation. His verbalization is to say that, for example, O in H_2O is *negativ zweiwertig*, enforcing a view that *wertigkeit* still is a plain number to which a + or − sign can be attached. Nernst in "Theoretische Chemie"[21] p. 386 keeps strictly the conservative view "…Ionen, welche mit der gleichen menge von Elektrizität geladen sind, wie das Wasserstoff- oder Chlorion, nennen wir einwertige…" (…ions charged with the same amount of electricity, such as hydrogen- or chlorine-ions, are 1-*wertige*…). In 1915, Fry published "The electronic conception of positive and negative valences".[22] Gilbert Lewis also wrote about valence, in 1913 and 1916.[23,24] In "The atom and the molecule",[24] he introduced a predecessor of the octet rule, the "theory of a cubical atom" to account for what had become known

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[3] In the article, the term "valenz" appears once; in the sense of bonding with specific amount of atoms. The number of such bonds at the P atom is then given by numerical adjectives with "werthig".

[4] Some recent historical accounts erroneously conflate the Werner's 1893 approach with his later textbook approach by equating the secondary valence with coordination number. The IUPAC Red Book[15] p. 144 has it correctly.

as “Abegg’s law of valence and countervalence”,[16] in which the total difference between the maximum negative and positive valences (or polar numbers) of an element is frequently eight and in no case more than eight.[5] In 1918, Joel Hildebrandt in his “Principles of Chemistry”[25] states on p. 85 “…we must … distinguish between two kinds of valence … by calling one positive and the other negative” and illustrates this by many examples, like “In Al_2O_3, the valence of Al is 3, because the valence of oxygen is –2” on p. 86. On p. 98, Hildebrandt lists the adjectives *n*-valent with either Greek or Latin prefix for positive *n* (not for negative valences) in a nomenclature suggestion.

By 1920, two types of valence as a numerical variable were in use; the polar number (valence) of positive or negative sign (also termed electrochemical valence or electrovalence[26]) and the stoichiometric valence (the maximum number of hydrogen atoms that may combine with an atom of the element under consideration). Both were colliding with the term valence as a description of bonding, and that conflict afflicted the German term *Valenz* as well. In a book, “Chemische Valenz-und Bindungslehre”,[27] Fritz Ephraim commented that “die Valenz Zahl und nicht etwa Kraft ist” (valence is a number not some force), here quoted from a series of historical sketches by Arthur Berry[28] p. 177. The terms polar number or polar valence number dominated in articles around this time. In 1927, yet another valence interpretation appeared in the book “The electronic theory of valency” by Sidgwick[29] with absolute valency defined on p. 182 as the number of electrons of the atom engaged in attaching the other atoms, quoting Grimm and Sommerfeld.[30] [6]

In the 1930s, the (polar) valence was replaced in two papers by Arthur Noyes et al. on “argentic salts” by the “state of oxidation”[31] or “oxidation state”.[32] Here, it may be noted that the term “state of oxidation” apparently first appeared in a 1901 paper by Leonard Morgan and Edgar Smith on chalcopyrite.[33] In 1938, Wendell Latimer published his groundbreaking book on redox half-reaction electrochemical potentials listed as a function of the oxidation state: “The Oxidation States of the Elements and their Potentials in Aqueous Solutions”,[34] where he used “oxidation state” and “oxidation number” as established terms. He considered them synonymous with German *wertigkeit* that he understood to mean “valence or polar number.” In 1940, a revised edition of Latimer and Hildebrand’s “Reference Book of Inorganic Chemistry” was published.[35] In its Glossary, the terms oxidation state or oxidation number are defined as “The charge on a simple ion or for a complex ion or molecule: the charge which is assumed on an atom to account for the number of electrons involved in the oxidation (or reduction) of the atom to the free element.” The same year, Joel Hildebrand’s 4th edition of “Principles of Chemistry” has oxidation number or state, stating explicitly on p. 120 that these replace the earlier term valence.

In 1941, IUPAC issued its first set of rules for naming inorganic compounds and writing their formulas[36] with the electrochemical valence [sic] following the atom symbol or name as a roman numeral inside bracket. For redox aspects, the term “valency stage” emerged, with a synonym “oxidation stage” for oxygen compounds. By 1948, oxidation state (or oxidation number) is used instead of the original valency.[37,38] At the 14th IUPAC general assembly in 1947 London, Linus Pauling presided over section II of the Congress. In the same year, he published a paper “The modern theory of valency”[39] advocating the need to “dissociate the concept of valency into several new concepts; *ionic valency*, *covalency*, *metallic valency*, *oxidation number*.” He compares the bonding aspect of valency with these numerical values. Thus, about ionic valency he argues that the actual ionic charges in an ionic compound are smaller than their ionic valency given by the positive and negative ionic charges (analogously for the numerical value of covalency). He then states that the positive and negative valences have a special redox nature that justifies designating them by the name oxidation number and proceeds to state four rules for its values. With such a more precise term now available, Pauling wonders “whether the word valency, without qualification, need ever be used.” His answer “I think that it may be used as a synonym for one of the more precise concepts when its meaning is clear from the context. Thus, in the classification of the compounds of iron, we may include the ferrocyanides among the compounds of bivalent iron…” is his suggestion to use it as an adjective for oxidation number if the context is clear. He concludes the paper[39] by a statement on valency as a concept of computation-based bonding theory: “If scientific progress continues, the next generation may have a theory of

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[5] Lewis places the electrons in the outer shell of the elements lithium to fluorine at the corners of a cube and points out that he presented this approach in a memorandum dated March 28, 1902.

[6] “Valenzzahlen = Anzahl der Elektronen, die zur Herstelung der Bindung beansprucht werden.”

valency that is sufficiently precise and powerful to permit chemistry to be classed along with physics as an exact science."

From the 1950s onward, the concept of numerical valence has not changed much. As the noun valence denotes ability, its numerical adjective *n*-valent sounds natural for simple counts. In inorganic chemistry, it occasionally expresses the oxidation state, a term without such adjective. In physical organic chemistry, the definition in the IUPAC Recommendation[1] entered the current IUPAC Gold Book: "The maximum number of *univalent* atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted." Another suggestion appeared in 1995, when Green[40] outlined the Covalent Bond Classification (CBC) for coordination compounds with the recycled term "valency number" in the Werner sense [13] as a number of bonding pairs formed by sharing electron from both atoms. In 2006, Parkin[41] prefers "valence" according to the 1927 Sidgwick[29] suggestion that never took off; the number of an atom's electrons in bonds. The CBC movement revised its "valence number" definition to the Parkin's one[41] around 2010 in an array of articles.[42–45] In 2022, the "Glossary of terms used in physical organic chemistry"[46] defined valence as the "Maximum number of single bonds that can be commonly formed by an atom or ion of the element under consideration." The adjective "commonly formed" takes the focus from the actual atom in a given compound to the element in general and involves a degree of opinion that is arguably inconsistent with anything definitional.

As for valence-history studies, in 1952, C. A. Coulson published a book titled "Valence".[47] A 1965 book by W. G. Palmer "A history of the concept of valency to 1930"[48] is an extended version of his lecture notes for a short course on valence at Cambridge University. A few years later, in 1971, Colin Russell published his four-part book "The history of valence".[49] The Part 1 deals with origins, nomenclature, and notation. Part 2 describes the structure applications of valence. Part 3 focuses on variations in valence and Part 4 on valence versus electric charge, up to wave mechanics. In 2005, Smith[50] in the paper "Valence, covalence, hypervalence, oxidation state, and coordination number" dealt with historical aspects of valence and similar terms. In 2015, Nelson gave an account of terms related to valence in his article "Modern version of Lewis's theory of valency".[51]

3 The current use of the term valence

The term valence enters some chemistry concepts, but it can also denote a quantity. The relative proportion of these two aspects of its use can only be estimated. We approached it by searching chemistry textbooks. The result shows that the use of the word valence as a quantity is minor compared with its use in chemistry-related non-quantitative concepts, and it differs between organic and inorganic chemistry.

3.1 Valence in textbooks

Thirty-three chemistry textbooks in English, covering general-, inorganic-, inorganic structural-, organic-, bioinorganic-, organometallic-, supramolecular-, physical-, materials-, and quantum-chemistry fields, were searched for each individual valence-containing or valence-derived term to find its number of occurrences in the text (not on the header or in any Index or Table of Contents). The search formulation included plurals and adjectives. Quantity terms *n*-valen(t, ce, cy) were searched separately for each *n*. When valence was defined in the book, we searched the numerical values attached to valence and added them into the statistics. Outcomes from advanced inorganic-, organic-, and physical-chemistry textbook are in Table 1.

The numerical adjective of valence (*n*-valent) does not occur often. The 12 times use in a book in Table 1 is one of the highest, besides two other textbooks with 11 and 13 cases. No such adjective occurs in 13 of the 33 investigated textbooks. The inorganic chemistry book of Table 1 uses *n*-valent 3 times while the oxidation state appears 578 times in quantitative context. The organic chemistry book with 12 uses of *n*-valent gives the oxidation state quantity 4 times (another 4 have a vague general context). In the physical chemistry book, *n*-valent appears 5 times while oxidation state 18 times.

Table 1: Frequency of terms in "Physical Chemistry" by Atkins 8th ed. (2006), 1040 pages; in "Inorganic Chemistry" by Housecroft and Sharpe, 3rd ed. (2008), 1042 pages; and in "Organic Chemistry" by Wade, 6th ed. (2006), 1261 pages.

The valence term in chemistry book	Physical	Inorganic	Organic
Covalent(ly)	44	154	45
Valence electron(s)	14	149	34
VSEPR (valence shell electron-pair repulsion)	1	92	2
Valence bond	20	40	1
Covalency (degree of)	0	1	0
Covalence	0	0	0
n-Valent (*n* is a specific integer)	5	3	12
Valence shell(s) not referring to VSEPR	9	35	13
Valence energy or level	0	0	0
Hypervalence and hypervalent	0	15	0
Mixed valence and mixed valent	1	12	0
Valence orbital	3	19	0
Low valent	0	1	0
High valent	0	0	0
Valence odd, even… (if valence is defined in the book)	–	–	3
Valence with a numerical value (if valence is defined in the book)	–	–	5

3.2 Valence terms of quantitative context

To approach various perceptions of valence as a quantity and use them thereafter, we summarized our own agreed-upon understanding of current use of the quantity-related valence terms at the time of writing (with no intention to replace any existing IUPAC Recommendations or definitions). The three following subsections are arranged by increasing quantitative context:

3.2.1 Nouns with "valence" that are countable

Some terms containing valence refer to familiar countable objects. Such countable entities "valence-something" add a dimension to the meaning of the word valence:

Valence orbitals are those an atom can use for making bonds via sharing its electrons (while leaving some of them nonbonding in the given set of *s*, *p*, and *d* orbitals) and via "accepting" "donated" electron pairs. Their count develops down the Periodic Table to the final configuration at each period as follows:

Period 1:	s	1 valence orbital (1*s*)
Period 2:	sp^3	4 valence orbitals (2*s* and 2*p*)
Period 3:	sp^3	4 valence orbitals (3*s* and 3*p*)
Period 4:	d^5sp^3	9 valence orbitals (4*s*, 3*d*, and 4*p*)
Period 5:	d^5sp^3	9 valence orbitals (5*s*, 4*d*, and 5*p*)
Period 6:	d^5sp^3	9 valence orbitals (6*s*, 5*d*, and 6*p*)

For lanthanoids, the submerged 4*f*-shell makes the term valence orbitals vague and rarely used. Likewise with actinoids in period 7.

Valence electrons are atom's own electrons in valence orbitals of the given group of the Periodic Table. They control chemical properties. The valence-electron count N of a chemical element follows most easily from the group numbering in the IUPAC Periodic Table. Up to group 10, the number of atom's valence electrons equals the group number. From groups 12 to 18, the number of valence electrons equals the group number minus 10. Group 11 is intermediate and behaves as if this count varied with the compound type, for Au being affected also by relativistic effect[52] (Section 10.4).

Valence pairs are valence-electron pairs that either bond one atom with another or are present as lone pairs[53] (p. 4). This term has evolved into "valence electron pairs" or "electron pairs".

3.2.2 Quantitative context but no numerical value

The root "valence" appears in several terms with a general quantitative context yet no numerical value as such. Adjectives *n*-valent, high-valent, or low-valent do not apply here as they refer to specific values for a given atom or element.

Hypervalence or **hypervalent** may refer to *sp*-block atoms having more bonds than valence orbitals *s* and *p*, as in PCl_5 or in SF_6 described in Section 10.1, or entering stoichiometries that violate octet or 8–N rule at this *sp*-block central atom, such as $HClO_2$, $HClO_3$, $HClO_4$, and many others.[54] Thus, Cavallo et al.[55] use "hypervalent" for halogen atoms that "form more than one covalent bond". Jackson et al.[56] avoid hypervalence by counting 4 covalent bond pairs at the *sp*-block atom, of which some or all overlap with ionic interaction. Already in 1960, Pauling[57] (p. 9) used formal charges to explain the N–O bond strength in $(CH_3)_3NO$. In "Glossary of terms used in theoretical organic chemistry" IUPAC Recommendation 1999[58] on p. 1946, hypervalence is defined as the ability of an atom in a molecular entity to expand its valence shell beyond the limits of the Lewis octet rule.

Hypovalence or **hypovalent** refers to molecules where a main-group element has a surrounding of seven or less valence electrons (not satisfying the octet rule).[59]

Polyvalence or **polyvalent** refers to an atom that has valence greater than two, or it refers to an atom able to adopt several valences in its compounds.

Isovalent refers in general to valence being equal for two atoms of two different elements in their specific bonded state, typically when comparing two compounds. In extended structures/solids (non-molecular solids of periodic networks in at least one dimension), a term popularized by Hughbanks and Hoffmann,[60] it often appears as "isovalent substitution", where one element replaces another of the same ionic charge.

Aliovalent is the opposite of isovalent.[61] When used for extended solids, it refers to substitution of one element for another that changes the ionic charge at the site (e.g., Riess in Tuller and Balkanski[62] on p. 28).

Heterovalent is synonymous with "aliovalent". Heterovalent substituents enter lattice position normally occupied by ions of different charge[63] (p. 124).

Sub-valent refers to compounds in which fewer bonds are formed than "valence rules" suggest, such as PH_2 in Atkins and Overton[64] p. 266.

Semi-valent refers to an element/atom involved in a two-center one-electron bond (a bond between two atoms with only one electron shared). It may also denote the ability of an atom to form a one-electron bond.[65]

Expandable valence is a property of a central atom to form compounds in which it becomes hypervalent. It is also used as "expandable valence shell" that refers to compounds such as PF_3 of that atom able to "expand valence shell" by forming PF_4^-.

Saturated valence refers to the maximum valence quantity of a central atom, for example, along the BF_3, $SiCl_4$, PCl_5, and SF_6 arrays.

Intervalence (charge transfer) refers to a compound where atoms of the same metallic element differ only in their oxidation state, a "mixed valence compound" defined[66] by Robin and Day. Rather than a quantity, intervalence is an adjective to the charge transfer (induced thermally) between the non-equivalent metal centers, as in a 1996 IUPAC Recommendation "Glossary of terms used in photochemistry"[67] p. 2248.

High or low covalence refer to the degree of covalence as a fraction or percentage of covalent character of a generally ionocovalent bond (every ionic bond has a covalent component, not vice versa).

Primary and secondary valences are described in Section 1. They appear in about 3000 science articles as adjectives (secondary-valence bond, force, band, cross-links, linkage, interactions, and networks) to describe the bonding type, a concept, not a quantity.

3.2.3 Composed "valence" terms that have a numerical value

Besides the term valence itself and its direct numerical adjectives (monovalent, divalent, etc.), several composed terms are in use that have a numerical value.

Mixed valence (adjective **mixed-valent**) refers to a chemical element as if adopting two or several different oxidation states in a compound; fully separated (class I), or distinguishable (class II), or fully merged into one single average value (class III).[66,68] The merged mixed valence may occur between atoms in an extended solid or in a molecular structure, even if mediated by a bridge, such as in the Creutz–Taube complex $[(NH_3)_5Ru(NC_4H_4N)Ru(NH_3)_5]^{5+}$ of two equivalent Ru atoms linked by pyrazine.[69] The term "mixed valence" refers to the oxidation state of that element. The numerical values are conveyed by the oxidation state or ionic charge such as the $Fe^{2.5+}$ fully merged in $YBaFe_2O_5$[70] above 312 K, or the Fe^{3+} and Fe^{5+} fully separated in $CaFeO_3$ at 4 K,[71] or $O_2{}^{2-}$ and $O_2{}^{-}$ present in Rb_4O_6.[72]

Bond valence[73] has the same meaning as the term bond order in molecules, only that it is typically used for extended structures (networks) of crystalline non-metallic solids, where it is calculated from the bond length to a value more or less approaching the ideal bond order in the given structure. See Karen et al.[74] p. 1024 for a short overview with more details and references on this concept.

Electrovalence (ionic valence) in Merriam-Webster[75] is "Valence characterized by the transfer of one or more electrons from one atom to another with the formation of ions (as in sodium chloride and other simple salts). Also, the number of positive or negative charges acquired by an atom by the loss or gain of electrons." Electrovalence(y) is a counterpart of the covalence(y).[76] The electrovalence can also be defined as positive or negative;[77,78] hence, the formulation can include the **formal charge** at an atom in a Lewis formula of a molecule or ion. However, the electrovalence remains ambiguous as it typically refers to ionic bonds, while about a century ago it meant a quantity we now know as oxidation state.[26]

Magnetic valence as a quantity was briefly used to approximate the saturated moment in Bohr magnetons of Fe, Co, and Ni alloyed with near-neighbor metals; $2N_d{}^{\uparrow} - N$.[79] Since the number of majority-spin *d*-electrons $N_d{}^{\uparrow} = 5$ per atom is constant, the term was somewhat superfluous. As an adjective before band, state, or model, it appears in physics.

3.3 Survey on valence as a quantity

One of the most important criteria behind IUPAC normative work is reflectivity; the adopted standards should reflect the current use as much as possible. The survey among 28 chemists from IUPAC divisions to assign quantity values of valence in about 20 examples of simple molecules or ions had twofold purpose: (1) Identify possible valence concepts behind the obtained span of numerical values for a given example. (2) Convert answers of each participant into preference for the valence concept behind these quantities without having to ask to state it directly or formulate a definition. The consistency (in %) of the given respondent's use of each particular concept was then evaluated. The results confirm that the perception of valence as a quantity concept is widely divergent (Table 2).

Table 2: Quantity concept behind valence values and number of respondents with most answers pointing to it in general (A) or only if the respondent's consistency for that concept was >50 % (B).

The valence-quantity concept	A	B
Number of bonding electron pairs at an atom	11	9
Number of bonding pairs sharing electrons of both atoms	6	4
Oxidation state	5	5
Number of electrons an atom uses in bonds	4	5
Number of bonded nearest neighbors	2	2
Absolute value of oxidation state	0	1

4 Possible definitions of valence as a quantity

The quantity concepts identified in the survey (Section 3.3) are candidates for the definition of valence as a quantity. Two other quantity concepts of valence, not discerned in the survey, were added; the current IUPAC definition of valence[1] and the bond-valence (bond-order) sum at an atom. As the quantities are often determined on a Lewis formula, a complementing concept of formal charge at the atom was included, which also covers ionic charges.[7] Fig. 1 illustrates these quantities on a Lewis formula of carbon monoxide, where each dash represents an electron pair. As we are about to test these quantities via their verbal definition or algorithm, we will keep referring to them by their explanatory names. In tables, we will use suitable shorthand to avoid needless inventing of symbols. An explanatory list of these quantities (in bold) with some verbal algorithms follows.

The **number of electrons an atom uses in bonds**[29] was suggested[41] in 2006 as a definition of valence and later on used by the related group of authors as "valence number".[42,45] On a Lewis formula, it is counted as the number of an atom's valence electrons that are not in the essentially nonbonding "lone pairs".

The **number of bonding pairs at an atom** or **co-valence**[8] is a formal number of predominantly covalent bonding-pair equivalents counted on the formula. In Fig. 1, it corresponds to the number of dashes denoting a two-electron bonding orbital, but in structures of other compounds it can be a sum of bond-order fractions. The co-valence does not include ionic interactions via electrons not drawn on the formula of an isolated cation or via electrons already bonding inside the formula of an isolated central-atom ion.

The **formal charge**, a form of electrovalence,[9] is obtained on a Lewis formula by bisecting all bonds and counting the resulting charge at each atom. In Lewis formulas of neutral molecules, formal charges compensate each other, as in Fig. 1. Carbon monoxide indeed has an experimental dipole moment[80,81] with its negative end at the carbon atom, and the actual bond order is about 2.6.[82] [10] The formal charge at an atom depends on the setup of the Lewis formula. The formula may indeed be drawn to obey the 8–N rule (Section 10.1) that originates

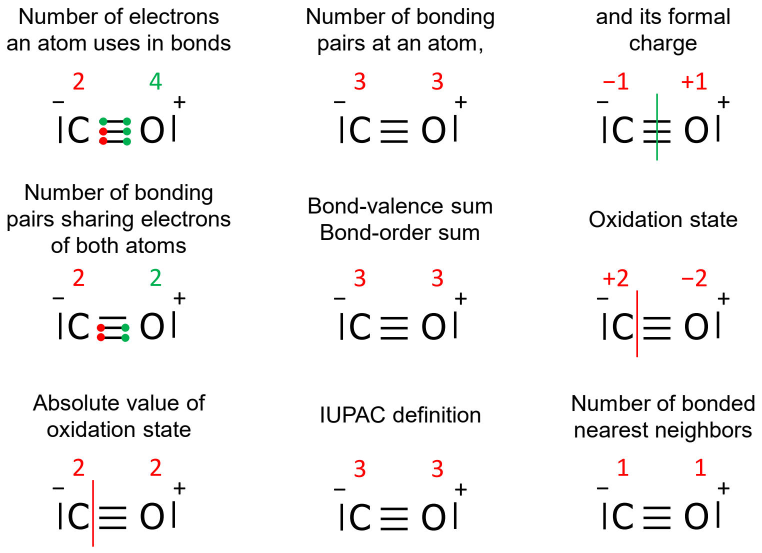

Fig. 1: Quantities tested as definitions of valence (and the formal charge) illustrated on octet-obeying Lewis formula of carbon monoxide with triple-bond approximation that yields non-zero formal charges.

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[7] Accordingly, in formulas and figures, the formal charge will appear like ionic number, whereas the quantity value in the text and equations as a positive or negative number with sign.

[8] We'll spell this alternative term with hyphen, because the quantity name covalence often refers to a degree or fraction of covalent character in an ionocovalent bond (as noted in Section 3.2.2).

[9] In this context, we'll spell it as electro-valence, in analogy to co-valence.

[10] If the more electropositive atom has a negative formal charge, the effect is antibonding. Negative formal charge at the more electronegative atom generates ionic-bonding effect (Pauling[57] p. 9).

with Hume-Rothery:[83] An *sp*-block atom of N valence electrons tends to form $8 - N$ two-electron bonds with atoms of equal or lower electronegativity.[11] While formal charges on isolated single-atom anions are trivial in this aspect, for oxo-anions, or anions with electronegative ligand atoms in general, it is more realistic to apply the 8–N rule. The anion formula is then drawn with all ligand-atoms' ionocovalent bonds as dashes with denoted bond order. It keeps all formal charges zero on the formula of that isolated anion and its bond orders close to reality (see Fig. 6).

The **number of bonding pairs sharing electrons of both atoms** is the valence of the Werner[13] type, obtained by summing bond orders of such bonds at the atom in the given formula. It requires attention to avoid counting donated bonding pairs.

The **bond-valence sum**[73] or **bond-order sum**[74] (p. 1029) is a sum of bond valences (Section 3.2.3) or bond orders at an atom. The former is used on bond graphs (Section 4.2) of extended structures, and the latter term may better suit molecules. At times, idealized representations occur. For bond graph, see Fig. 9; for idealized Lewis formula of a molecule, see Figs. 1 and 2.

The **oxidation state** of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds.[84] Besides direct ionic approximation limited to simple formulas[74] (p. 1025), two general algorithms, subject to a caveat, calculate its quantity value[84] using the Allen-electronegativity criterion. Algorithm 1: Oxidation state equals the charge of an atom after its homonuclear bonds have been divided equally and heteronuclear bonds assigned to the more electronegative bond partners. Electronegative atom bonded *reversibly* as a Lewis-acid ligand (electron-pair acceptor) does not obtain that bond's electrons. Algorithm 2: The sum of heteronuclear bond orders by their polarity sign at the atom, plus any formal charge on that atom. For electronegative atom bonded *reversibly* as a Lewis-acid ligand (electron-pair acceptor), the formal bond polarity is inverted. Both algorithms work fine on CO of Fig. 1. After assigning bonds, C has a lone pair, the two electrons of which we subtract from the $N = 4$ valence electrons of C to yield the oxidation state +2. Oxygen has 8 electrons, the subtraction of which from $N = 6$ gives the oxidation state −2. In the second algorithm, the positively taken bond order at C is summed with the formal charge −1 to +2, and the negatively taken bond order at O is summed with +1 to −2. Direct ionic approximation on CO formula yields the same.

The **absolute value of oxidation state** might better resemble valence. The term valence is rarely used for negative values.

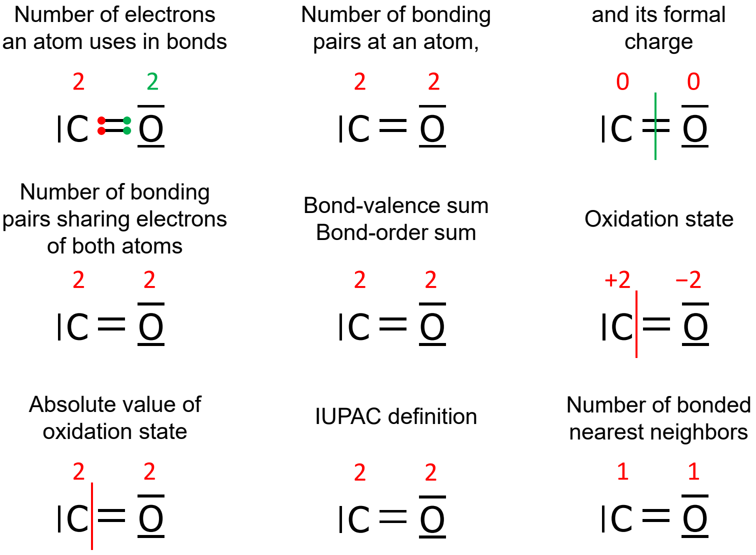

Fig. 2: Quantities tested as definitions of valence (and the formal charge) evaluated on a Lewis formula of carbon monoxide that complies with both octet rule and 8–N rule.

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[11] The 8–N rule is not necessarily identical with the octet rule. One or the other is violated on Lewis formulas $|N{\equiv}N^{+}{-}\,\overline{O}|^{-}$ and $|N{\equiv}N{=}\,\overline{O}$.

The present **IUPAC definition** of valence (Section 1) is tricky on the Lewis formula of Fig. 1. It asks us to find maximum number of univalent atoms that combine with an atom of *the element under consideration*. In our Lewis formula, that certainly is not a plain carbon as an element in general. We ask, what is the bonding state (electron configuration) at our atom under consideration in the Lewis formula? The carbon under consideration is $|C^-$. It may combine with 3 H into the carbanion $|CH_3^-$. Likewise, the $|O^+$ may combine with 3 H into the oxonium cation $H_3O|^+$. Hence, both valences are 3. See also Sections 5.1 and 5.3.

The **number of bonded nearest neighbors** is an explanatory description of the common term coordination number.

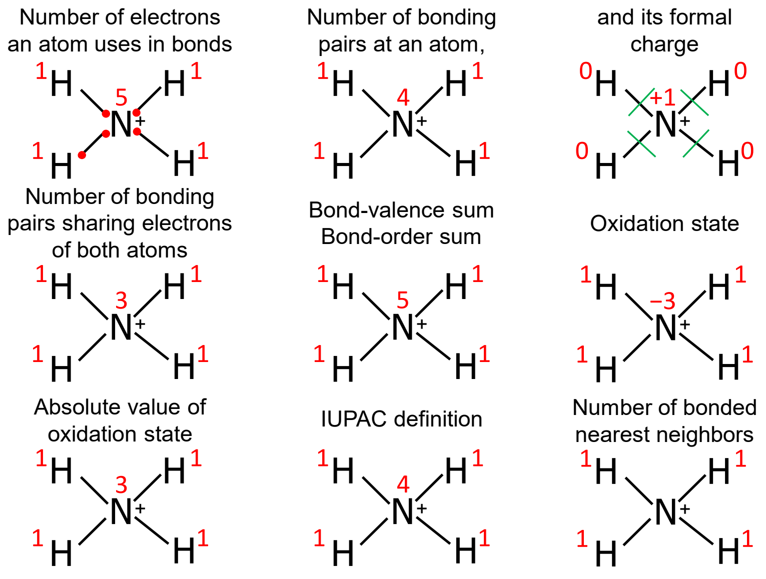
While the Lewis formula in Fig. 1 nicely illustrates all valence-type quantities considered here, it is not the only one possible. Applying the 8–N rule to CO, we limit the number of bonds at the most electronegative atom, oxygen, to two, as the oxygen atom lacks only two electrons to obtain its stable configuration. Such a formula simplifies the results obtained for the “valence” quantities on CO. The number of electrons the atom uses in bonds is “per definition” the one dictated by this 8–N rule (Fig. 2). It is also equal to the number of two-electron bonds at the atom. The formal charge is zero on both atoms. As no bonds are donated, the (formal) number of electron pairs sharing both atom’s electrons equals the number of bonding pairs at the atom; the bond-valence (bond-order) sum likewise. The oxidation state naturally remains the same. As mentioned earlier in this Section, the reality of the CO molecule is a compromise between the Lewis formulas in Figs. 1 and 2.

4.1 Applied on Lewis formulas of ions of several atoms

As illustrated above in the example of CO with formal charges, the quantity values depend on whether the chemical bonding formula respects the 8–N rule or not. Figs. 3 and 4 illustrate this fact on two limiting Lewis formulas for the NH_4^+ cation and Figs. 5 and 6 for the BF_4^- anion.

4.1.1 Ammonium cation

The Lewis formula of NH_4^+ that respects the octet rule is drawn in Fig. 3 with four bond dashes of the available 8 valence electrons. The number of electrons nitrogen uses in bonds is 5 (nitrogen’s valence electrons minus the 0 in lone pairs). The number of bonding electron pairs at nitrogen is 4 (the co-valence, so we do not include the ionic bonding), and its formal charge is +1 (the electro-valence). Each hydrogen uses 1 electron in bonds, considering


Number of electrons an atom uses in bonds

Number of bonding pairs at an atom,

and its formal charge

Number of bonding pairs sharing electrons of both atoms

Bond-valence sum Bond-order sum

Oxidation state

Absolute value of oxidation state

IUPAC definition

Number of bonded nearest neighbors

Fig. 3: Quantities tested as definitions of valence (and the formal charge) on conventional Lewis formula of NH_4^+ that disrespects the 8–N rule.

that the proton accepting the nitrogen pair has arisen from an H atom that used its electron to bond the unexpressed anion (e.g., Cl^-). We see one bonding pair at each H and hence zero formal charge.

On the second row left, only 3 bonding pairs at N atom share electrons of both atoms; one pair is donated. As the formal ionic charge 1+ resides on N that already has sp^3 configuration, one can argue against counting this ionic bond as an ionocovalent shared pair on nitrogen. Prior forming the NH_4^+, the fourth H atom became the Lewis-acid H^+ by giving an e^- to form an anion (e.g., Cl^-). One might argue that the Cl^- remains bonded to the + charge by hydrogen's electron and that could justify the valence 1 at that fourth H atom in this formula that leaves the anion unexpressed. This Lewis formula is somewhat unclear on this particular definition of valence.

The bond-valence (bond-order) sum on nitrogen in this formula is 5, composed of 4 single bonds to H and 1 ionocovalent bond of the + ionic charge with any number of close contacts to unexpressed anions totaling 1– ionic charge. A hypothetical purely ionic bond of 1+ and 1– charges is a two-electron bond (physically located at the unexpressed anion in this ionic extrapolation). The oxidation state of N is –3 by both algorithms (Section 4): The 8 electrons around N of 5 valence electrons yield –3. The sum of negatively taken four single-bond orders plus the formal charge N^+ yields –3 as well. So does the direct ionic approximation performed on the NH_4^+ formula.

On the third row, the present IUPAC definition of valence (Section 1) is as if already applied in this four-bonded N^+ combined with 4H, hence tetravalent. The last value, the number of nearest bonded neighbors of H atoms in this formula is 1, as this quantity remains uncertain on N because we consider the cation as isolated and do not know the number of neighbors.

The problems encountered in Fig. 3 vanish on the other limiting Lewis formula that respects both the octet and the 8–N rule (Fig. 4). It has fractional bond orders labeled on the dashes. We count 8 valence electrons per NH_4^+ but demand that nitrogen only uses 3 electrons for bonding; hence, the bond order is ¾. That is not far from reality, as the N–H bond length 0.988 Å (98.8 pm) obtained by neutron diffraction on crystalline hydrogen-bonded ND_3 at 77 K[85] increases to 1.042 Å (104.2 pm) at 80 K in ND_4NO_3.[86]

The number of electrons nitrogen used in bonds equals the number of atom's valence electrons minus those in nonbonding pairs. In this formula, it is dictated by the 8–N rule on nitrogen. Hydrogen used ¾ of an electron to bond N and ¼ to bond the unexpressed anion. The number of bonding electron pairs (co-valence) at nitrogen is 3 whereas ¾ at the hydrogens where we do not include the ionic bonding. The formal charge (electro-valence) at the electronegative nitrogen atom is 0 per the 8–N rule and ¼ of the ionic charge at each hydrogen.

The formal number of bonding pairs that share electrons of both bonded atoms is 3 at nitrogen and 1 at hydrogen, composed of ¾ of an electron shared with N and ¼ shared with the unexpressed anion, say Cl^-, as there

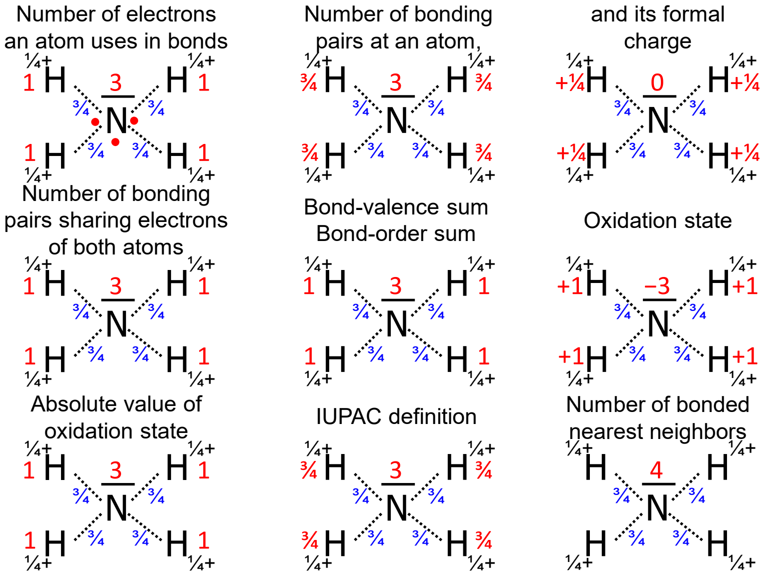


Fig. 4: Quantities tested as definitions of valence (and the formal charge) on a limiting Lewis formula of NH_4^+ that obeys octet rule as well as the 8–N rule (bond orders are in blue).

is no such thing as a purely ionic bond. The bond-valence sum concerns all ionocovalent interactions, hence 3 at nitrogen and 1 at hydrogen.

Oxidation states obtain by either of the two algorithms. Hydrogen: First algorithm leaves H with no electrons and +1 oxidation state. Second algorithm sums the bond orders ¼ and ¾ at this electropositive atom to the oxidation state +1. Nitrogen: First algorithm takes the octet at N and obtains oxidation state as 5 – 8 = –3. Second algorithm sums the bond orders to –3. The present IUPAC definition of valence (Section 1) applies to nitrogen with one lone pair and bond-order total 3. Such |N≡ would bond 3 hydrogens. With how many Cl would hydrogen of ionic charge ¼+ bond? With ¾ Cl to $(\mathrm{HCl}_{3/4})^{1/4+}$. Nitrogen has 4 nearest bonded neighbors. With hydrogen we do not know.

4.1.2 Tetrafluoridoborate(1−) anion

The Lewis formula for BF_4^- of 32 electrons that respects only the octet rule (and has the 1– ionic charge unlikely placed at boron) is in Fig. 5. The evaluations are as follows:

Boron uses 3 own electrons in bonds with 3 F that each uses 1 electron. How many electrons did the fourth fluorine use? Upon formation of this anion from the BF_3 Lewis acid and F^- Lewis base, the latter donated 2 electrons, but one of them (yellow, Fig. 5) it obtained from the unexpressed cation-forming element (e.g., $K \rightarrow K^+ + e^-$). Hence, also the fourth F atom used just 1 own electron (green). The simple way to count this quantity is as the atom's valence electrons minus those in the atom's nonbonding pairs.

Boron has 4 bonding electron pairs that represent its co-valence; hence, we do not include the ionic bonding via its formal charge –1 due to electrons that already bond B and F. Formal charges obtain by bisecting all bonds, summing electrons in adjacent halves to each atom, and subtracting that sum from the valence-electron number of that atom. Fluorine has 1 bonding electron pair and formal charge zero.

The number of two-electron bonds sharing electrons of both atoms is simple to check on the boron that shares all 3 of its electrons and was donated one bond. One F atom formed the Lewis-base F^- with electron from K that became K^+. The F^- then donated one electron pair with one own (thus shared) electron to B. The K^+ keeps its ionic bond to the 1– charge of that donated pair. With sp^3 configuration at B, one can argue against counting this ionic bond as a fifth ionocovalent shared pair on boron.

While the sum of bond valences at each F is 1 single bond, the boron has two sets of ionocovalent bonds: 4 single bonds to the F atoms and the ionocovalent contacts to the unexpressed cations (in the crystal or solution) that total to bond order 1. The oxidation state is straightforward both by assigning bonds to the electronegative fluorine or by summing the formal charge with the sum of bond orders taken positively at B and negatively at F. So is the direct ionic approximation on BF_4^- of 32 electrons forming octets at F. The present IUPAC definition of valence (Section 1) is straightforward in this Lewis formula; a single bond on F suggests 1 while the B^- bonding to 4 fluorine atoms gives 4. The coordination number we see only at the boron atom, and only if we neglect the "ionic" bonds to its unexpressed cation neighbors.

The problems of the Lewis formula in Fig. 5 vanish upon respecting electronegativity (fluorine atoms must carry the anion charge and ionocovalent bonds) and applying the 8–N rule. The result is in Fig. 6.

In this formula of the anion, the number of electrons the atom used in bonding (*N* valence electrons of the element minus those in nonbonding pairs) and the co-valence (number of two-electron bonds) are the same. All formal charges (electro-valence) are zero because the 32 electrons of the anion include those that make the ionocovalent bonds to the unexpressed cation, and one obtains 7 – [6 + ¼ + ¾] = 0 at F and 3 – 4 × ¾ = 0 at B.

The formal number of bonding pairs sharing electrons of both bonded atoms is 1 at fluorine (¾ of an electron shared with B and ¼ shared with the unexpressed K^+ cation as there is no such thing as a purely ionic bond) and 3 at boron (4 × ¾) = 3. As all bonds are drawn, the bond-valence sums give the same values. The oxidation state by assigning bonds is straightforwardly 3 for boron of no electrons after all bonds are assigned to fluorine that obtains –1 by subtracting electrons in bonds assigned to it from its number of valence electrons, 7 – [6 + 2 (¾ + ¼)].

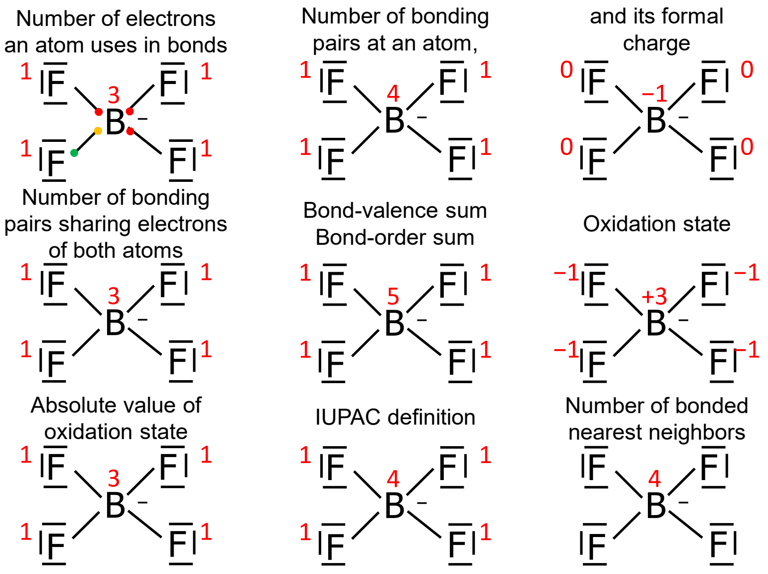


Fig. 5: Quantities tested as definitions of valence on octet-obeying Lewis formula of BF_4^-.

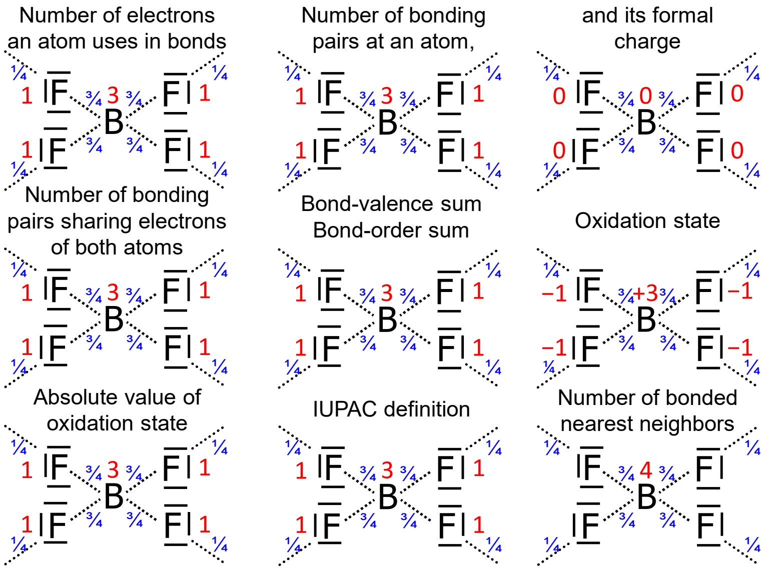


Fig. 6: Quantities tested as definitions of valence on Lewis formula of BF_4^- that obeys the octet rule as well as the 8−N rule (bond orders are in blue).

The present IUPAC definition of valence (Section 1) is straightforward here as the B fragment of no nonbonding electrons would bond with 3 Cl atoms (per the definition), and fluorine with 3 lone pairs and total bond order 1 would bond 1 H. The coordination number of boron is 4 in the tetrahedron but remains uncertain at fluorine since we artificially consider an isolated anion.

4.2 Applied on bond graphs of extended solids

A bond graph is a finite representation of an extended (non-molecular) solid,[87,88] a bonding formula of the crystal. On the periodic unit of suitably distributed atoms, one draws a line for each instance of direct bonding connectivity between near-neighbor atoms in the structure. The line does not have the meaning of a two-electron bond; it carries the specific bond order defined by the chemical element and the local symmetry that controls the connectivity. Such a bond order is called bond valence (Section 3.2.3). Two examples of extended solids follow.

4.2.1 Cesium trioxidoiodate

The crystal structure of this salt has an infinite network of $IO_{6/2}^-$ octahedral anions with dodecahedral voids filled by Cs^+. Its cubic perovskite cell in Fig. 7 shows that iodine coordinates 6 oxygens of the anion, while the $CsIO_3$ formula requires that the bond-order sum on iodine is 5. Each Cs^+ bonds to 12 iodate oxygens, and its bond-order total must equal 1. The bond graph on the right visualizes the bond-valence sums at each atom. The valence-type quantities derived on this bond graph are in Fig. 8. For oxidation state, the ionic approximation applies in the bond-order summing (with the + sign on Cs and I and with the − sign on O). We see that, except for the coordination number, all alternative valence definitions yield the same absolute value.

4.2.2 Calcium dicarbide

In the densest-packed Ca^{2+} spheres and C_2^{2-} ellipsoids of the CaC_2 crystal, calcium is coordinated by 8 carbons at a distance of 2.83 Å and by 2 carbons at 2.55 Å[89] (Fig. 9). Because of the two different calcium–carbon distances, there is no unique set of idealized bond orders, but a simple approximation helps: A bond-order calculation by the bond-valence method[90] from the above bond distances suggests the longer distance to be about half the bond order of the shorter distance. With this condition and bond order 3 in the C_2^{2-} anion, the idealized bond graph in Fig. 9 has one Ca–C bond of order 1/3 and four of order 1/6, summing with 3 to the total 4 at C.

The quantity values derived by counting on the bond graph in Fig. 9 are in Fig. 10. Because Algorithm 2 does not count homonuclear bonds, the oxidation state of carbon now differs from the other quantities. What could make the bond-valence sum differ from the number of electrons the atom uses in bonds? Dative bonds in the network, formed by electrons of the sole donor (see overview in Table 11 of Appendix A). What could make the bond-valence sum differ from the number of bonding pairs at the atom? The single ionic bond of “conventional” formulas for NH_4^+ (Fig. 3) and BF_4^- (Fig. 5) ions, which counts into the bond-valence sum at the central atom but not into its co-valence. No such features appear in the CaC_2 bond graph in Fig. 9.

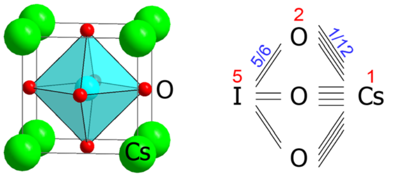


Fig. 7: Cubic unit cell of the perovskite-type $CsIO_3$ structure and its bond graph with bond orders (in blue) summing to the expected total (bond-valence sum, in red).

Number of electrons an atom uses in bonds 1 5 2 Cs I O_3	Number of bonding pairs at an atom, 1 5 2 Cs I O_3	and its formal charge 0 0 0 Cs I O_3
Number of bonding pairs sharing electrons of both atoms 1 5 2 Cs I O_3	Bond-valence sum 1 5 2 Cs I O_3	Oxidation state +1 +5 −2 Cs I O_3
Absolute value of oxidation state 1 5 2 Cs I O_3	IUPAC definition 1 5 2 Cs I O_3	Number of bonded nearest neighbors 12 6 6 Cs I O_3

Fig. 8: Valence-type quantities derived from the bond graph of $CsIO_3$ perovskite in Fig. 7.

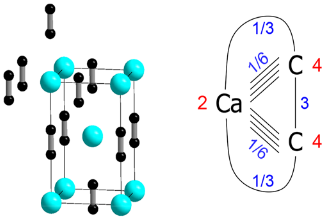


Fig. 9: Unit cell of CaC_2 with added anions to see the Ca^{2+} coordination (left). Bond graph of idealized bond orders (in blue) into bond-valence sums (in red).

Number of electrons an atom uses in bonds 2 4 $Ca\,C_2$	Number of bonding pairs at an atom, 2 4 $Ca\,C_2$	and its formal charge 0 0 $Ca\,C_2$
Number of bonding pairs sharing electrons of both atoms 2 4 $Ca\,C_2$	Bond-valence sum 2 4 $Ca\,C_2$	Oxidation state +2 −1 $Ca\,C_2$
Absolute value of oxidation state 2 1 $Ca\,C_2$	IUPAC definition 2 4 $Ca\,C_2$	Number of bonded nearest neighbors 10 5 $Ca\,C_2$

Fig. 10: Quantities tested as definitions of valence on the bond graph of CaC_2 in Fig. 9.

4.3 A case with Lewis-acid ligand

This rare case is illustrated by a complex of the Au central atom bonded to Cl and a tridentate ligand of aromatic rings and four isopropyls (Fig. 11), synthesized from AuCl-based precursor and the ligand molecule.[91] The central atom has an unusual combination of bonding; one bond it shares, one bond it donates to Lewis-acid B, and two it accepts from Lewis-base P in ClAu[(B⋲)(P⋲)$_2$] with bond triplets to carbons. Fig. 12 illustrates evaluation of the first three valence-type quantities that also relate to each other; on Lewis formulas, the number of electrons an atom uses in bonds equals the number of bonding pairs on it plus its formal charge.

The other three valence-type quantities are in Fig. 13. Due to dative bonds, the number of bonding pairs via sharing electrons of both atoms is low. The bond-valence (bond-order) sum corresponds to the number of bonding pairs at each atom in Fig. 12. How to apply the current IUPAC definition of valence (Section 1) on the “element under consideration”? The four-bonded P^+ of the Lewis formula in Fig. 11 would combine with 4 H to PH_4^+. Analogously, the four-bonded B^- would combine with 4 F to BF_4^- and the four-bonded Au^- with 4 F to AuF_4^-.

The oxidation state is obtained by ionic extrapolation via Allen electronegativity (in the so-called Pauling units, symbol PU in Mann et al.[92]) of Au, B, P, C, and Cl = 1.92, 2.051, 2.253, 2.544, and 2.869, respectively, listed also in

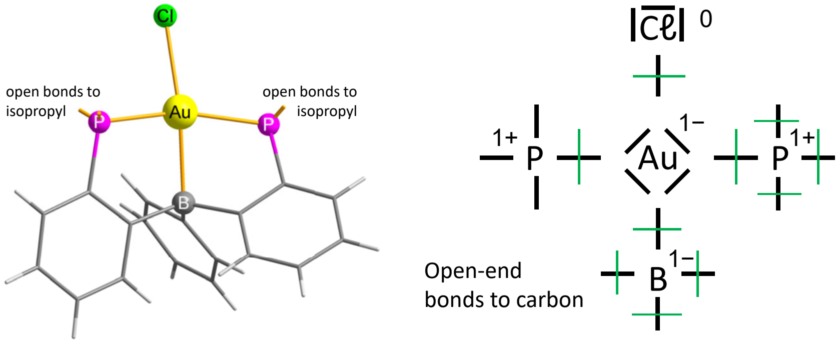


Fig. 11: The complex with relevant segment ClAu[(B⋲)(P⋲)$_2$] of two Lewis-base P donors and one Lewis-acid B acceptor (left). Lewis formula with formal charges counted upon bisecting bonds (right).

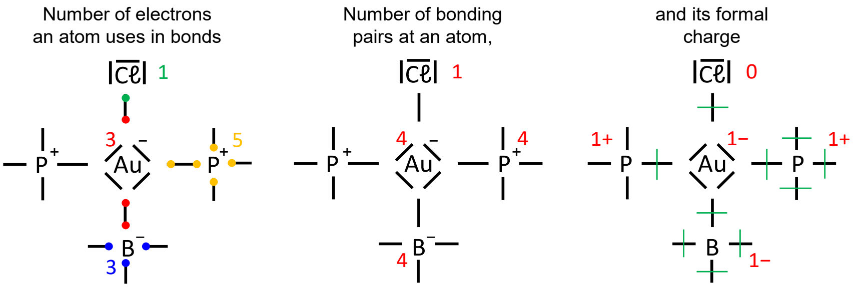


Fig. 12: The ClAu[(B⋜)(P⋜)$_2$] of three bond types. First three valence-type quantities.

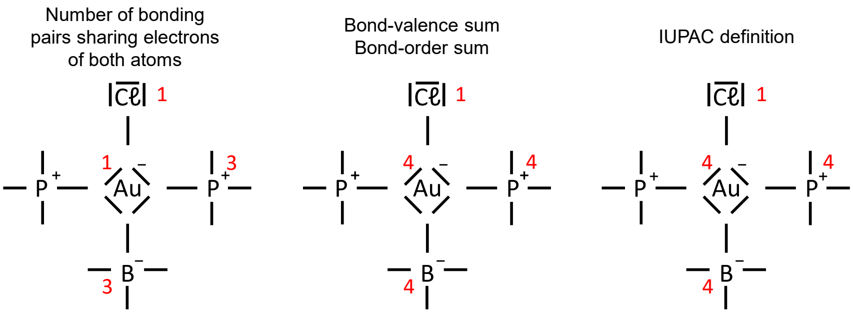


Fig. 13: The ClAu[(B⋜)(P⋜)$_2$] of three bond types. Second three valence-type quantities.

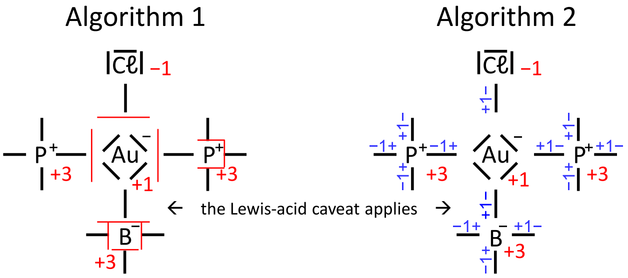


Fig. 14: The ClAu[(B⋜)(P⋜)$_2$] of three bond types. Oxidation state (red) by assigning bonds or by summing bond orders (blue) with formal charge (black), both by allen electronegativity with the Lewis-acid caveat (Section 4) applied on boron.

Karen et al.[84] The ligand-exchange synthesis from AuCl(H_3C–S–CH_3)[91] and the stable tridentate ligand of the product suggest application of the caveat of the electronegative Lewis-acid ligand (Section 4) for boron in the Au–B bond. Both algorithms yield the same oxidation states in Fig. 14.

5 Example pairs and current use of valence in them

In many of the evaluated example compounds, the quantities calculated with the alternative valence definitions had different values. Since reflection is important principle of the IUPAC normative work, we analyzed how the alternative definitions reflect the current, even if relatively modest, use of the term valence in English. For each of such telling examples, we asked the following question: Do chemists say that an atom in this compound is *k*-valent or *l*-valent or *m*-valent? The answer was obtained with Google Scholar search at several geographical locations (somewhat different results) for articles in which we then analyzed the context of each adjective *n*-valent with common variants of the prefix *n*, such as di- and bi- or tetra- and quadri-.

5.1 $HgCl_2$ and Hg_2Cl_2

The quantity values obtained by testing the alternative definitions of valence on $HgCl_2$ and Hg_2Cl_2 are compared in Table 3 of columns that follow the order in Fig. 8. Counting all valence quantities is straightforward. That also

Table 3: Valence-type quantities for $HgCl_2$ and Hg_2Cl_2.

$\lvert\overline{\underline{Cl}}-Hg-\overline{\underline{Cl}}\rvert$	#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
Hg	2	2	0	2	2	+2	2	2	2
Cl	1	1	0	1	1	−1	1	1	1
$\lvert\overline{\underline{Cl}}-Hg-Hg-\overline{\underline{Cl}}\rvert$	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**$\lvert OS\rvert$**	**IUPAC**	**CN**
Hg	2	2	0	2	2	+1	1	2	2
Cl	1	1	0	1	1	−1	1	1	1

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence); f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state.

concerns the present IUPAC definition of valence in the 1994 Recommendation on "physical organic chemistry" terms,[1] where every carbon atom counts separately, and so does Hg in Hg_2Cl_2.

Our question about the current use was: As mercury in $HgCl_2$ is divalent, do chemists say that Hg_2Cl_2 has divalent or monovalent mercury? The search shows that nobody says that mercury in Hg_2Cl_2 is divalent. In 24 papers, it is stated as a compound of monovalent mercury.

5.2 CH_4 and C_2H_2

A similar comparison deals with two simplest organic molecules (Table 4). With the auxiliary formal charge zero, the single heteronuclear bonds in CH_4 yield the same absolute value for all remaining quantities. In C_2H_2 of one triple bond, the oxidation state differs even in its absolute value.

The actual use of "*n*-valent" is of interest here. While carbon in CH_4 is clearly tetravalent, do chemists say that carbon in C_2H_2 is monovalent or tetravalent? The answer is unambiguous: In all searched organic-chemistry references, carbon in C_2H_2 is stated as tetravalent because it forms four two-electron bonds.

5.3 $Cr_2(CH_3COO)_4$ and CrO_3

The paddlewheel molecule of dichromium(II) tetraacetate dihydrate crystal is in Fig. 15 left, without the two H_2O molecules weakly bonded to Cr along the wheel axis. The $Cr–OH_2$ bond-order contribution is 0.22 by bond-valence calculation of O'Keeffe and Brese[90] from atomic coordinates in the crystal, published by Cotton et al.,[93] where the water bonds two other paddlewheels by a hydrogen bond of O···O distance 2.84 Å (284 pm). The paddlewheel

Table 4: Valence-type quantities for CH_4 and C_2H_2 molecules.

CH_4	#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
C	4	4	0	4	4	−4	4	4	4
H	1	1	0	1	1	+1	1	1	1
C_2H_2	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**$\lvert OS\rvert$**	**IUPAC**	**CN**
C	4	4	0	4	4	−1	1	4	2
H	1	1	0	1	1	+1	1	1	1

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence) f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state.

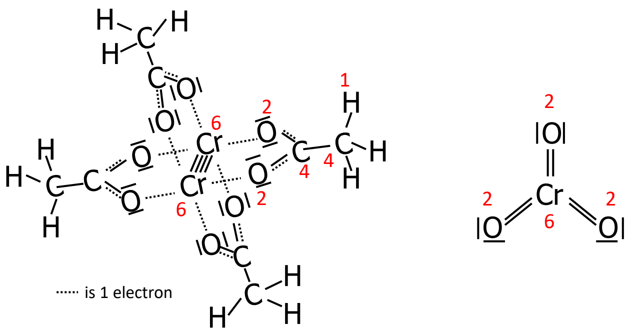


Fig. 15: Lewis formulas of dichromium(II) tetraacetate molecule of 104 valence electrons and of CrO_3 with 12 electron pairs. The numbers of electrons the atom uses in bonds are in red.

Table 5: Valence-type quantities evaluated on dichromium(II) tetraacetate and CrO_3 Lewis formulas in Fig. 15.

Cr(II) acetate	#e	#bp	f.c.	#p.sh.	BVS	OS	|*OS*|	IUPAC	CN
Cr	6	6	0	6	6	+2	2	6	5
O	2	2	0	2	2	−2	2	2	2
C carboxyl	4	4	0	4	4	+3	3	4	3
C methyl	4	4	0	4	4	−3	3	4	4
H	1	1	0	1	1	+1	1	1	1

CrO_3	#e	#bp	f.c.	#p.sh.	BVS	OS	|*OS*|	IUPAC	CN
Cr	6	6	0	6	6	+6	6	6	3
O	2	2	0	2	2	−2	2	2	1

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence); f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state.

molecule is highly symmetrical as all carbon–oxygen distances are the same and so are all chromium–oxygen ones. It is compared with another wheel, CrO_3, in Fig. 15 right.

Table 5 lists quantity values obtained by testing the alternative definitions of valence on the two formulas of Fig. 15. The results are self-explanatory. The present IUPAC definition of valence refers to each Cr atom's 6 two-electron bonds that would bond 6 Cl.

The relevant question was: While chromium in CrO_3 is hexavalent, do chemists say that dichromium(II) tetraacetate dihydrate has divalent or hexavalent chromium? The answer was simple. Nobody says that Cr in dichromium(II) tetraacetate is hexavalent. In five papers, it is divalent, in one of those in a similar compound. In additional 14 papers, other compounds of Cr^{II} are described as divalent. See also overview of these comparative examples in Table 10.

5.4 ReF_7 and $ReCl_3$

Halogenides of second- and third-row transition metals form often molecular or network solids. Two such examples are compared here. While ReF_7 is a molecule of a shape close to trigonal bipyramid,[94] $ReCl_3$ is a crystalline solid of Re_3 clusters bonded to Cl, bridged by Cl, and joined with other clusters by Cl into a 3D network.[95] The network repeat unit in Fig. 16 also lists the bond lengths. Bond-valence calculation with parameters of O'Keeffe and Brese[90] from the actual bond lengths yields the following bond-order estimates for the chlorine bridges (for the nomenclature μ convention, see Connely et al.[15] p. 208). The sole Cl–Re "μ_1" bond has bond order 1.137, each Cl–Re bond of μ_2 bridges on Re–Re edges has 0.800, and the μ_2 bridges between repeat units have one Cl–Re bond order 0.785 and the other 0.442. The >1 bond-order sum of bridging halogens justifies the standard electron counting by two-electron bonds. Counting electrons at the Re_3 cluster of the $Re_3Cl_6Cl_{6/2}$ repeat

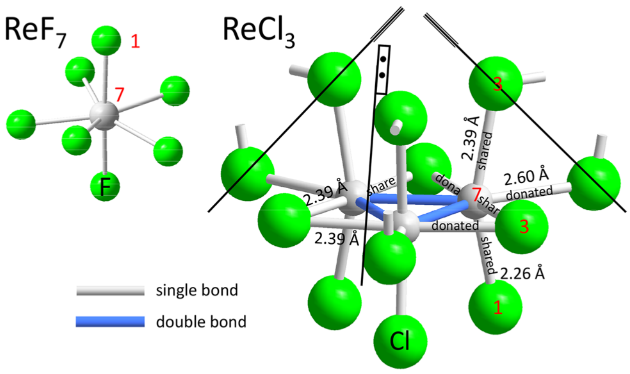


Fig. 16: Repeat units of solid ReF_7 on left and $ReCl_3$ on right, the latter with rounded off bond distances (1 Å = 100 pm) and identification of single bonds as via electrons shared with or via both electrons donated by the bridging ligand. The cluster triangle is in blue. Numbers of atom's electrons used in bonds are in red.

unit via "neutral atoms" (Housecroft and Sharpe[96] p. 815) yields 21 electrons from three Re, 3 electrons from the three single-bonded Cl, 3 (2 + 1) = 9 electrons from the three μ_2 bridges on the Re_3 edges, and 6 (2 + 1)/2 = 9 electrons from the six inter-unit bridges. In total, 21 + 3 + 9 + 9 = 42 electrons. With $g = 42$ for the $n = 3$ Re atoms, the generalized 18-plet formula for clusters, $N_{\mathrm{BO}} = (18n - g)/2$ derived in Section 10.6, yields six orbitals that bond the Re_3 cluster of 18-plet at each Re. The Re_3 cluster has double bonds. All other bonds are single bonds in this approximation.

With the Fig. 16 of single Re–Cl bonds and double Re=Re bonds, it is not too difficult to derive the set of valence-type quantities (Table 6) as done in the first paragraphs of Section 4. Let's take a few:

The formal charge: The single-bonded chlorine has formal charge 0. The two single bonds of bridging Cl we cut in half giving the atom two electrons and formal charge 7 – (4 + 2) = +1, where $N = 7$, and four electrons are in nonbonding pairs on Cl. Bisecting bonds around Re gives it 4 + 5 = 9 electrons and formal charge 7 – 9 = –2.

The oxidation state by Algorithm 1 is the charge at the atom after ionic approximation by assigning bond electrons to the partner of higher Allen electronegativity and dividing homonuclear bonds equally. In the Fig. 16 approximation, Re loses the 3 electrons it shares with Cl but keeps the 4 shared with the two other Re, and $OS_{\mathrm{Re}} = 7 - 4 = +3$. The Cl gains all electrons in bonds, and $OS_{\mathrm{Cl}} = 7 - 8 = -1$. The oxidation state by Algorithm 2 is the sum of the atom's heteronuclear bond orders by their polarity sign at the atom, summed with any formal charge on that atom. Hence, the five heteronuclear bonds sum as +5 on Re of formal charge –2, and the $OS_{\mathrm{Re}} = 5 - 2 = +3$. Single-bonded chlorine of formal charge 0 has $OS_{\mathrm{Cl}} = -1 + 0 = -1$, and the bridging chlorine of formal charge +1 sums up its two single bonds as –2, and $OS_{\mathrm{Cl}} = -2 + 1 = -1$. Direct ionic approximation on ReF_3 is straightforward.

With the present IUPAC definition of valence (Section 1), we ask: What is the state (electron configuration) at our atom under consideration and how would it bond with F or H? Rhenium of formal charge –2 and 9 two-electron bonds would be in ReF_9^{2-}. The single-bond counting on Cl is straightforward with 1 as in HCl and 2 on the bridging Cl, as the $-\overline{\underline{\mathrm{Cl}}}-$ corresponds to ClF_2.

Table 6: Valence-type quantities for $ReCl_3$ (repeat unit Re_3Cl_9) and ReF_7 in Fig. 16.

$ReCl_3$	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
Re (of 3)	7	9	–2	7	9	+3	3	9	7
μ_1 Cl (of 3)	1	1	0	1	1	–1	1	1	1
μ_2 Cl (of 6)	3	2	+1	1	2	–1	1	2	2
ReF_7	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
Re	7	7	0	7	7	+7	7	7	7
F (of 7)	1	1	0	1	1	–1	1	1	1

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence); f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state.

The question about the current use was: The rhenium in ReF_7 is heptavalent; do chemists say that $ReCl_3$ has trivalent, heptavalent, or nonavalent rhenium? Nobody says that solid $ReCl_3$ has a heptavalent or nonavalent rhenium. In seven papers, Re is stated as trivalent in $ReCl_3$. See also overview of these comparisons in Table 10.

5.5 $MoCl_6$ and $MoCl_2$

Likewise, we compare the $MoCl_6$[97] molecule with an extended solid $MoCl_2$[98] Counting electrons at the Mo_6 cluster of the $Mo_6Cl_{10}Cl_{4/2}$ repeat unit via "neutral atoms" starts with 36 electrons from six Mo and 2 electrons from the two single-bonded Cl atoms. Then, 6 electrons are added from the four inter-unit μ_2 bridges counted per the repeat unit as 4/2 = 2 Cl atoms sharing 1 and donating 2 electrons. The μ_3 bridges on the eight faces of the Mo_8 octahedron add 40 electrons (5 electrons from each Cl, 1 shared and 4 donated). In total, 36 + 2 + 6 + 40 = 84 electrons. With g = 84 for the n = 6 Mo atoms, the formula $N_{BO} = (18n - g)/2$ derived in Section 10.6 yields 12 orbitals bonding the 12 edges of the Mo_8 cluster having 18-plet on each Mo. All bonds in the repeat unit are therefore single bonds.

With all bonds single in this approximation, the valence-type quantities in Table 7 are straightforward. In $MoCl_2$ of Fig. 17, the numbers of electrons that the atom uses in bonds verbalize as follows: The "μ_1" Cl shares 1 and donates 0; the μ_2 Cl shares 1 and donates 2; the μ_3 Cl shares 1 and donates 4. Molybdenum uses all its valence electrons.

The formal charge is zero for the two single-bonded Cl atoms. The μ_2 Cl atom has two lone pairs of 4 electrons and obtains 2 electrons from bisecting its two bridging bonds, hence 7 – (4 + 2) = +1. The μ_3 Cl atom has one lone pair of 2 electrons and obtains 3 electrons from bisecting its 3 bridging bonds, 7 – (2 + 3) = +2. Bisecting all nine bonds around Mo gives it 9 electrons, and 6 – 9 = –3 for its formal charge. These charges per neutral formula

Table 7: Valence-type quantities for $MoCl_2$ (repeat unit Mo_6Cl_{12}) and $MoCl_6$ in Fig. 17.

$MoCl_2$	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
Mo (of 6)	6	9	–3	6	9	+2	2	9	9
μ_1 Cl (of 2)	1	1	0	1	1	–1	1	1	1
μ_2 Cl (of 2)	3	2	+1	1	2	–1	1	2	2
μ_3 Cl (of 8)	5	3	+2	1	3	–1	1	3	3
$MoCl_6$	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
Mo	6	6	0	6	6	+6	6	6	6
Cl (of 6)	1	1	0	1	1	–1	1	1	1

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence); f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state.

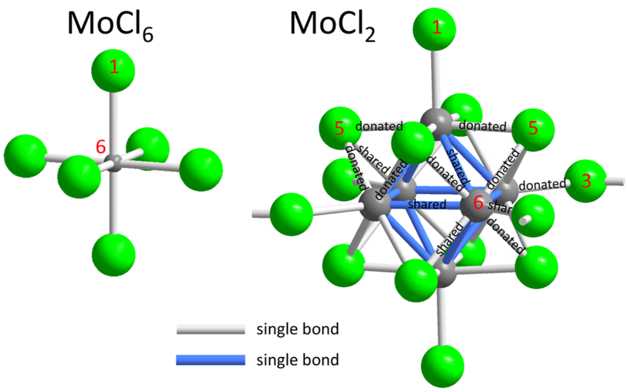


Fig. 17: Repeat units of solid $MoCl_6$ on left and $MoCl_2$ on right. Numbers of atom's electrons used in bonds are in red. The cluster octahedron is in blue.

sum to zero: The 12 Cl atoms per repeat unit have total formal charge 0×2 and $+1 \times 2$ and $+2 \times 8$ equal +18, and the six Mo atoms have -3×6 equal −18.

The oxidation state via Algorithm 1: By ionic approximation, Mo loses 2 electrons it shares with Cl yet keeps the 4 it shared with four other Mo; $OS_{\mathrm{Mo}} = 6 - 4 = +2$. Single-bonded Cl gains all electrons in bonds and $OS_{\mathrm{Cl}} = 7 - 8 = -1$. Algorithm 2: The polarity-weighted sum of the atom's heteronuclear bond orders plus any formal charge gives +5 for Mo of formal charge −3, and $OS_{\mathrm{Mo}} = 5 - 3 = +2$. Single-bonded chlorine of formal charge 0 has $OS_{\mathrm{Cl}} = -1 + 0 = -1$. The μ_2 Cl atom of formal charge +1 sums up the two bridging single-bond orders 1 as −2 and its $OS_{\mathrm{Cl}} = -2 + 1 = -1$. The μ_3 Cl atom of formal charge +2 sums up the three bridging single bonds as −3 and its $OS_{\mathrm{Cl}} = -3 + 2 = -1$. Direct ionic approximation on $MoCl_2$ is straightforward.

What is the state (electron configuration) at one Mo atom "under consideration" and how would it bond with F or H? Such an Mo of formal charge −3 with 9 two-electron bonds would be in MoF_9^{3-}. That gives valence 9 for Mo by the present IUPAC definition of valence. The single-bonded Cl yields 1, the μ_2 Cl yields 2 as the $-\overline{\underline{\mathrm{Cl}}}-$ configuration corresponds to ClF_2, and, likewise, the μ_3 Cl configuration corresponds to ClF_3.

The number 9 appearing among the quantities for Mo may appear extreme. Is it an artifact of the 18-plet counting or is there a reality behind the 9? An estimate of bond orders from interatomic distances in the crystal by Schäfer et al.,[98] calculated according to O'Keeffe and Brese,[90] gives 8.62 for the bond-order sum at the two apical Mo atoms, 8.39 at the four equatorial Mo atoms, 0.76 at the single-bonded Cl, 1.07 at the inter-cluster μ_2 Cl, and 1.85 for the μ_3 Cl. That largely justifies the cluster bonding idealized with single bonds, while indicating that the inter-cluster Cl bridges might be just two one-electron bonds.

We asked the following question: With Mo in $MoCl_6$ always referred to as hexavalent, do chemists say that $MoCl_2$ has divalent, hexavalent, or nonavalent molybdenum? The answer was simple; nobody says $MoCl_2$ has hexavalent or nonavalent molybdenum. In eight papers, Mo is divalent in this chloride. In additional four papers, similar Mo-cluster complexes are described as of divalent Mo. See also overview of such comparisons in Table 10.

5.6 Ni(C≡O)$_4$ versus Ni(C=O)$_4$

Tetracarbonylnickel forms from Ni and CO. Table 8 illustrates the subtle difference the 8−N rule makes for the valence-type quantities evaluated on two alternative Lewis formulas in Fig. 18, each of 25 electron pairs. Nickel uses zero electrons in bonds and has 4 bonding pairs. With 10 electrons in nonbonding pairs, the Ni formal charge is $10 - (4 + 10) = -4$. There are 4 bonding pairs at Ni, and the sum of bond valences is also 4.

The oxidation state of Ni is zero by Algorithm 1 that assigns bonds to atom of higher Allen electronegativity and leaves Ni with 10 electrons in lone pairs. Or, by the second algorithm, the polarity-weighted sum of Ni heteronuclear bond orders gives +4 on Ni of formal charge −4, and $4 - 4$ yields oxidation state zero. Table 8 shows that the alternative formulas for the ligands give the same valence-tested quantities for the central atom Ni. The present IUPAC definition of valence for Ni atom "under consideration" follows from its state that tells how many F

Table 8: Valence-type quantities evaluated on alternative Lewis formulas of $Ni(CO)_4$ in Fig. 18.

Ni(C≡O|)$_4$	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
Ni	0	4	−4	0	4	0	0	4	4
C	4	4	0	2	4	+2	2	4	2
O	4	3	+1	2	3	−2	2	3	1
Ni(C= $\overline{\underline{\mathrm{O}}}$)$_4$	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
Ni	0	4	−4	0	4	0	0	4	4
C	4	3	+1	2	3	+2	2	3	2
O	2	2	0	2	2	−2	2	2	1

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence); f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state.

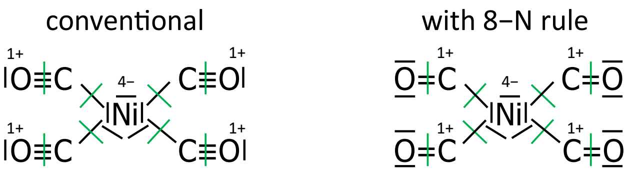


Fig. 18: Alternative Lewis formulas of tetracarbonylnickel with formal charges marked as counted within the green-line cuts.

Table 9: Sulfur valence-type quantities tested on Lewis formulas of SBr_2 versus S_2Br_2 and H_2S versus H_2S_2 molecules.

	#e	#bp	f.c.	#p.sh.	BVS	OS	|*OS*|	IUPAC	CN
SBr_2	2	2	0	2	2	+2	2	2	2
H_2S	2	2	0	2	2	−2	2	2	2
S_2Br_2	2	2	0	2	2	+1	1	2	2
H_2S_2	2	2	0	2	2	−1	1	2	2

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence); f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state.

or H it would bond. A d^{10} Ni, with four two-electron bonds and formal charge −4, would bond as in NiH_4^{4-}, hence valence 4. The C and O values would differ on the two formulas in Fig. 18.

We asked the following question: Do chemists say that tetracarbonylnickel has zero-valent or tetravalent Ni? The answer is that nobody says $Ni(CO)_4$ has tetravalent Ni. In 12 papers, Ni is zerovalent in this carbonyl. In additional five papers, Ni is considered zerovalent in this carbonyl, even with a small portion of the carbonyl ligands replaced with another electrically uncharged donor. In additional six papers, Ni is zerovalent in complexes where it bonds with three or four donor atoms of a neutral ligand into an uncharged complex. See also the overview of comparative examples in Table 10.

5.7 SBr_2 and H_2S versus S_2Br_2 and H_2S_2

The sulfur valences by the alternative definitions follow from the Lewis formulas $|\overline{\underline{\mathrm{Br}}}-\overline{\underline{\mathrm{S}}}-\overline{\underline{\mathrm{Br}}}|$ and $\mathrm{H}-\overline{\underline{\mathrm{S}}}-\mathrm{H}$ compared with $|\overline{\underline{\mathrm{Br}}}-\overline{\underline{\mathrm{S}}}-\overline{\underline{\mathrm{S}}}-\overline{\underline{\mathrm{Br}}}|$ and $\mathrm{H}-\overline{\underline{\mathrm{S}}}-\overline{\underline{\mathrm{S}}}-\mathrm{H}$ in Table 9. All bonds are by shared electrons, and all formal charges are zero. In SBr_2 and H_2S, sulfur is divalent by all definitions, only the latter oxidation state is negative. In S_2Br_2 and H_2S_2, the absolute value of the sulfur oxidation state becomes 1.

The question about the current use was: While sulfur in SBr_2 and H_2S is divalent, do chemists say that sulfur is divalent also in S_2Br_2 and H_2S_2? The answer is clear, 27 papers consider S divalent in S_2Br_2 and H_2S_2, of which 19 are by organic chemists and 8 by inorganic chemists. Additional four organic chemistry papers denote a sigma-bonded S radical monovalent, since it is bonded by one two-electron bond.

6 Relations among the tested quantities

All valence-type quantities tested in this study stand on their own as parameters that characterize some aspects of bonding. In this section, we list the main general relationships among the quantity values obtained on our 39 example entities and several types of chemical formulas or bonding schemes:

6.1 Ever-valid relations

(1) Application of the present IUPAC definition (Section 1) on the atom "under consideration" taken as a fragment with its bonds present in the given Lewis formula, by asking how many F or H it would bond, yields valence

identical to the number of two-electron bond equivalents drawn at it (see Table 11 in Appendix, definition columns: col.2 = col.8).

(2) On a full Lewis formula of a compound or ion: **The number of electrons an atom uses in bonds** = **the number of two-electron bonds on that atom** + **its formal charge on the Lewis formula** that may or may not follow the 8–N rule (Table 11 definition columns: col.1 = col.2 + col.3)[12]

(3) *N* valence electrons of an atom – those it uses in bonds = the number of essentially nonbonding electrons at that atom (see the nontrivial Au in Fig. 12).

6.2 More specialized relations

(1) The bond-valence (bond-order) sum at an atom equals the sum of that atom's two-electron bonds (co-valence) on Lewis formulas of neutral molecules or on bond graph of periodic networks[13]

(2) The sum of the atom's two-electron bonds (co-valence) obviously equals the number of bonds formed by sharing both atoms' electrons only if none of bonds at this atom is dative. Otherwise, absolute value of that atom's formal charge (electro-valence) must be added to its number of electron-sharing bonds to get its co-valence (see Table 11, definition columns: col.2 = |col.3| + col.4).

(3) The number of electrons an atom uses in bonds (Table 11, definition col.1) equals the number of bonds formed by sharing both atoms' electrons (Table 11 definition col.4) unless that atom also donates own electrons.

(4) The absolute value of the oxidation state (Table 11, definition col.7) and the number of electrons an atom uses in bonds (Table 11, definition col.1) are equal when all bonds at the given atom are heteronuclear, and the Lewis formula complies with the 8–N rule. In formulas not complying with the 8–N rule, these two quantities differ, such as in Fig. 1 on oxygen of the $|C{\equiv}O|$ molecule or in Table 8 on carbon and oxygen of $Ni(C{\equiv}O)_4$.

(5) Quantities behind the alternative definitions of valence are the same on binary compounds with electropositive atoms of no formal charge in a Lewis formula of heteronuclear single bonds such as H_2O, $HgCl_2$ (Table 3), SBr_2 (Table 9), and CH_4 (Table 4). See also overview in Table 11 in Appendix A.

(6) With the exception of coordination number, the valence-type quantities remain the same also when the electropositive central atom of no formal charge has bonds that are not single, such as CrO_3 in Table 5.

(7) Quantities by all tested definitions except coordination number and oxidation state are the same on all atoms in Lewis formulas where the 8–N rule was applied to remove formal charges and/or replace them with ionocovalent bonds: H_3O^+, NH_4^+ (Fig. 4), BF_4^- (Fig. 6), and CO (Fig. 2).

7 Summary of the current use of adjective *n*-valent in tested quantities

In Section 3, we concluded that the quantity term valence and its adjective *n*-valent are not used very often. Does their context imply that one of the investigated valence-type quantities prevails? In Section 5, we illustrated such current-use analysis with Google Scholar searches on eight examples of two compounds of the same element, where we could compare the preferred context of the adjective *n*-valent for chemists. Section 9 presents five more examples of a compound that yields high variation of the alternative valence quantities. The overview of the current use of *n*-valent on these telling examples is in Table 10.

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[12] With the alternative rarely used names, the CBC valence number[43] = co-valence[76] + electro-valence (formal charge).

[13] On Lewis formulas of ions, our co-valence does not count the formal charge (caused by bonds already there) as an additional ionic bond (on N in Fig. 3, on H in Fig. 4, on B in Fig. 5). Bond-valence sum in a crystal, on the other hand, is a sum of all bond orders at the atom (typically calculated from bond distances), and we counted all bond orders also in our Lewis formulas.

Table 10: Current use of the adjective *n*-valent on comparative examples.

1. Mercury in $HgCl_2$ is divalent:

Do chemists say that mercury is divalent in Hg_2Cl_2?								**#e**	**#bp**	**f.c**	**#p.sh.**	**BVS**	**OS**	**$\lvert OS\rvert$**	**IUPAC**	**CN**
Hg in Hg_2Cl_2	24	papers as	1	valent	No			2	2	0	2	2	1	1	2	2
	0	papers as	2	valent	No			2	2	0	2	2	1	1	2	2
In addition	26	papers merely confirm the presumption that mercury is divalent in $HgCl_2$ or in Hg^{2+}														

2. Carbon in CH_4 is tetravalent:

Do chemists say that carbon is tetravalent in C_2H_2?								**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**$\lvert OS\rvert$**	**IUPAC**	**CN**
C in C_2H_2	4	papers as	4	valent	Yes	4 organic		4	4	0	4	4	−1	1	4	2
	2	papers as	2	valent				4	4	0	4	4	−1	1	4	2
	0	papers as	1	valent				4	4	0	4	4	−1	1	4	2
In addition	35	papers consider C divalent when it has two bonding pairs, such as in carbenes														

3. Chromium in CrO_3 is hexavalent:

Do chemists say that Cr is hexavalent in chromium(II) acetate?								**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**$\lvert OS\rvert$**	**IUPAC**	**CN**
Cr in $Cr_2(CH_3COO)_4{\cdot}2H_2O$	0	papers as	6	valent	No			6	6	0	6	6	2	2	6	5
	4	papers as	2	valent	No			6	6	0	6	6	2	2	6	5
In a similar Cr_2 complex	1	paper as	2	valent	No			6	6	0	6	6	2	2	6	5
In addition	14	papers consider Cr in Cr^{II} compounds divalent														
	2	papers use *n*-valent for ionic charge of a Cr complex.														

4. Rhenium in ReF_7 is heptavalent:

Do chemists say that $ReCl_3$ has tri-, hepta-, or nonavalent Re?								**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**$\lvert OS\rvert$**	**IUPAC**	**CN**
Re in $ReCl_3$ or Re_3X_9	7	papers as	3	valent	↔			7	9	−2	7	9	3	3	9	7
	0	papers as	7	valent				7	9	−2	7	9	3	3	9	7
	0	papers as	9	valent				7	9	−2	7	9	3	3	9	7
In addition	1	paper uses valence as synonym for oxidation state even with negative values														
	2	consider Re trivalent in an octahedral complex with 3 Cl^- and 3 electron-pair-donor atoms														

5. Molybdenum in $MoCl_6$ is hexavalent:

Do chemists say that $MoCl_2$ has di-, hexa-, or nonavalent Mo?								**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**$\lvert OS\rvert$**	**IUPAC**	**CN**
Mo in $MoCl_2$	8	papers as	2	valent	↔			6	9	−3	6	9	2	2	9	9
	0	papers as	6	valent				6	9	−3	6	9	2	2	9	9
	0	papers as	9	valent				6	9	−3	6	9	2	2	9	9
In addition	2	papers consider similar Mo-cluster complexes that imply divalent molybdenum in $MoCl_2$														
	4	consider Mo divalent in an octahedral complex with $2Cl^-$ and 4 electron-pair-donor atoms														
	One	considers valence of the related $Mo_6Cl_{14}{}^{2-}$ anion to be its electrovalence (−2)														

6. Sulfur in H_2S is divalent:

Do chemists say that sulfur is divalent in H_2S_2?								**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**$\lvert OS\rvert$**	**IUPAC**	**CN**
S in H_2S_2 and R_2S_2	16	papers as	2	valent	Yes	8 org	8 inorg	2	2	0	2	2	−1	1	2	2
	Two	papers as	≠2	valent	No	1 org	1 inorg	2	2	0	2	2	−1	1	2	2
In addition	10	papers, all organic, merely confirm the presumption that one single –S– is divalent														
	4	all organic, use monovalent sulfur for radicals –S· with one sigma bond														
	1	uses “negatively bivalent” for S^{2-}														
	1	uses “bivalent” for $SO_4{}^{2-}$														
	4	use “monovalent sulfur vacancy” for point defect $V_S^{\cdot}$ in a solid (divalent for $V_S^{\cdot\cdot}$)														

Table 10: (continued)

7. Sulfur in SX_2 halogenide is divalent:

Do chemists say that sulfur is divalent in S_2X_2?								#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
S in S_2X_2	14	papers as	2	valent	Yes	11 org	3 inorg	2	2	0	2	2	1	1	2	2
	1	paper as	1	valent	No		1 inorg	2	2	0	2	2	1	1	2	2
	1	paper as	≠2	valent	No		1 inorg	2	2	0	2	2	1	1	2	2
In addition	8	papers, 7 organic, merely confirm the presumption that one single –S– is divalent														

8. Nitrogen in NH_3 is trivalent:

Do chemists say N in NH_4^+ formula of single bonds is tri-, tetra-, or hexavalent?								#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
N in NH_4^+	0	papers as	3	valent				5	4	1	3	5	−3	3	4	
	5	papers as	4	valent	↔			5	4	1	3	5	−3	3	4	
	0	papers as	6	valent				5	4	1	3	5	−3	3	4	
In addition	1	paper considers nitrogen in NH_4^+ negatively trivalent														
	2	refer to a ligand with six nitrogen donor atoms as hexavalent ligand														

9. Oxygen in H_2O is divalent:

Do chemists say O in H_3O^+ formula of single bonds is di-, tri-, or tetravalent?								#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
O in H_3O^+ or in R_3O^+	0	papers as	2	valent				4	3	1	2	4	−2	2	3	
	16	papers as	3	valent	↔	14 org	2 inorg	4	3	1	2	4	−2	2	3	
	0	papers as	4	valent				4	3	1	2	4	−2	2	3	
In addition	1	paper mentions divalent anion O^{2-}														
	1	considers three-connected O in TiO_2 network a trivalent oxygen														
	3	consider oxygen tetravalent in the hydrogen-bond network of solid or liquid water														

10. Do chemists say that carbon in the $\lvert C\equiv O\rvert$ formula is divalent or trivalent?								#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
C in $\lvert C\equiv O\rvert$	3	papers as	2	valent		1 org	2 inorg	2	3	−1	2	3	2	2	3	1
	1	paper as	3	valent		0 org	1 inorg	2	3	−1	2	3	2	2	3	1
In addition	10	inorganic papers have divalent C of two 2e bonds while not using any of its electrons														
	6	papers consider carbon divalent in the radical = C:														
	5	consider carbon trivalent in the radical ≡C														
	2	consider carbon trivalent in the $\equiv C\rvert^-$ anion														
	3	consider carbon trivalent in the $\equiv C^+$ cation														

11. Do chemists say that nickel in $Ni(CO)_4$ is zerovalent or tetravalent?								#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
Ni in $Ni(CO)_4$	12	papers as	0	valent	↔			0	4	−4	0	4	0	0	4	4
	0	papers as	4	valent				0	4	−4	0	4	0	0	4	4
In addition	5	papers consider nickel zerovalent in $Ni(CO)_{4-x}L_x^{donor}$														
	4	consider nickel zerovalent in a molecule where Ni bonds with 4 donor atoms														
	2	consider nickel zerovalent in a molecule where Ni bonds with 3 donor atoms														

12. Do chemists say that Mn in $Mn_2(CO)_{10}$ is zero-, mono-, or hexavalent?								#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
Mn in $Mn_2(CO)_{10}$	6	papers as	0	valent	↔			1	6	−5	1	6	0	0	6	6
	0	papers as	1	valent				1	6	−5	1	6	0	0	6	6
	0	papers as	6	valent				1	6	−5	1	6	0	0	6	6
In addition	1	paper considers manganese zerovalent in $Mn_2(CO)_8L_2^{donor}$														

13. Do chemists say that Os in $Os_3(CO)_{12}$ is zerovalent, divalent, or hexavalent?								#e	#bp	f.c.	#p.sh.	BVS	OS	$\lvert OS\rvert$	IUPAC	CN
Os in $Os_3(CO)_{12}$	9	papers as	0	valent	↔			2	6	−4	2	6	0	0	6	6
	0	papers as	2	valent				2	6	−4	2	6	0	0	6	6
	0	papers as	6	valent				2	6	−4	2	6	0	0	6	6

Table 10: (continued)

14. Do chemists say that nitrogen in N_2 gas is zerovalent or trivalent?				**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
N in N_2	2	papers as	0 valent	3	3	0	3	3	0	0	3	1
	1	Paper as	3 valent	3	3	0	3	3	0	0	3	1

15. Do chemists say that phosphorus in P_4 molecule is zerovalent or trivalent?				**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
P in P_4	4	papers as	0 valent	3	3	0	3	3	0	0	3	3
	1	Paper as	3 valent	3	3	0	3	3	0	0	3	3

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence); f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state; IUPAC = present IUPAC definition of valence; CN = coordination number of bonded atoms. Abbreviations: org = organic chemistry; inorg = inorganic chemistry.

The results show that inorganic chemists working with metals use *n*-valent as an adjective for positive oxidation states. Nobody uses any other alternative for *n*-valent metals in cases 1, 3, 5, 11, 12, and 13 listed in Table 10. On the other hand, organic chemists count *n*-valent as the number of bonding electron pairs at the atom. This follows from comparison of CH_4 and C_2H_2 (Section 5.2 and case 2 in Table 10) and from many more collateral statements in searched papers.

A conflicting use of *n*-valent appears on *sp*-block atoms. In clear-cut cases 8 and 9 in Table 10, every user of *n*-valent takes N in NH_4^+ as tetravalent and O in H_3O^+ as trivalent. Opinion is mixed about H_2S_2, S_2X_2, CO, N_2, and P_4 (respective cases 6, 7, 10, 14, and 15 in Table 10). Organic chemists still use *n*-valent here for the number of bonding pairs at the atom, and those few inorganic chemists who use *n*-valent in such molecular examples often take it as the oxidation-state in absolute value, but not all of them. In the rare papers that use *n*-valent for N_2, both zerovalent and trivalent N appear, while the heavier P_4 is mostly stated as zerovalent.

The diversity in use of *n*-valent has a cause. In organic chemistry, the current use corresponds to the current Gold-Book IUPAC definition of valence formulated in "Glossary of terms used in physical organic chemistry (IUPAC Recommendation 1994)".[1] It fits how organic chemists find the carbon valence 4 in CH_4 and C_2H_2 (Table 10 and Section 5.2) if the triple bond is taken as three single bonds. Likewise, chemists who work with *sp*-block nonmetals are often counting the actual number of single bonds, such as in the sulfur hydrides and bromides in Section 5.7 or in the NH_4^+ and H_3O^+ formulas (Table 10). Inorganic chemists working with metals follow the Pauling's suggestion for use of valence (see Section 2) as an adjective for oxidation state. As this feels natural only for positive oxidation states, terms "negative *n*-valent" are nearly absent in the literature.

8 Conclusions

The manifold context of valence as a quantity in the current use interferes with launching a single definition of valence. The situation is not much different from what Pauling describes in 1948.[39] The majority of the current and relatively infrequent use of "valence" as a quantity splits into two contexts of the adjective *n*-valent: (a) the number of two-electron bonds at the atom, typically of elements relevant for organic chemistry, and (b) the positive oxidation states of semimetals and metals. Already in 1913, Bray and Branch[19] suggested splitting the term "valence number" into "total valence number" in organic- and "polar valence" in inorganic chemistry. In addition to the two prevailing current uses, the CBC approach[14] has a "valence number" defined as the number of electrons an atom uses in bonds, following Parkin[41] who revived the 1927 suggestion by Sidgwick of absolute valency.[29] Unfortunately, this deviates from the above two current common understandings of valence as a quantity.

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[14] Search for articles with "valence number" and "CBC" gives 24 hits. Of these, 5 are by inventors of these terms, 4 are mere comment or mention, not use, and 13 have context irrelevant for valence number (4 use it for ionic charge) or for CBC. In 1 article and 1 thesis, these terms are actually used.

As these uses are bound to continue, clarity in communication is essential. It means stating what one means by valence via verbalizing the first use of valence quantity in organic chemistry or *sp*-block chemistry papers, or with an early-on specification that, say, divalent chromium is Cr^{2+} or chromium(II).

It would be worthwhile to alleviate the three problems of the current Gold-Book IUPAC definition of valence "The maximum number of *univalent* atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted": (1) Valence is defined with "valent." (2) The terms "element under consideration", "fragment", and "substituted" are not entirely clear. (3) The definition covers only a portion of the current use of valence as a quantity.

The problem (1) is easy to solve; the mentioned hydrogen atom clarifies that "univalent atom" has one two-electron bond. Naming fluorine instead of chlorine would strengthen this context if the "originally" were omitted. As for the problem (2) of the "element under consideration", "fragment", and "substituted", it is the atom's bonding environment that must be "considered" because valence is a quantity that always describes a bonded atom in a specific compound. The present IUPAC definition of valence then applies to that atom's bond-order total and its charge in Lewis formula, both of which we keep upon our thought bonding with "univalent" H or F. That **yields values identical to the often-used** (Section 7) **number of two-electron bonds or their equivalents at the atom**[15] (see Table 11). The problem (3) would be amended by stating the two different uses of valence as a quantity and emphasizing clarity in communications.

The 2022 "Glossary of terms used in physical organic chemistry" (IUPAC Recommendations 2021)[46] defines valence as the "maximum number of single bonds that can be commonly formed by an atom or ion of the element." Would it be 1 for halogens, 2 for chalcogens, 3 for pnictogens, and 4 for tetrels, as enforced by the 8–N rule when the element is the most electronegative bond partner? Or, is it 4 for all these, up to the octet limit? Or, could it be the saturated valence of the atom? What would the interpretation of "commonly formed" be for *d*-metals combining ionic and covalent bonding aspects?

There are two valence definitions in use over the main fields of chemistry, and they both concern the actual bonding of the atom in question. Only with that strict focus, the valence as a quantity, a chemical variable, becomes useful.

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[15] The latter quantity is at times termed "covalence" (in this text co-valence for clarity) and is zero for isolated cations M^{z+} of "electrovalence" z that we call ionic charge.

9 Appendix A: Overview of tested examples

Table 11 gives an overview of quantities derived on central atoms of majority of our tested examples of compounds represented by various types of formulas and variously applied stable-configuration rules. Details on important examples not described in the previous sections follow the table.

Table 11: Overview of important tested examples (co-valence = number of bonding pairs at the atom; electro-valence = formal charge on the Lewis formula; BVS = bond-valence or bond-order sum; OS = oxidation state; IUPAC = present IUPAC definition of valence; CN = coordination number of bonded atoms).

Unless specified otherwise, central atom or any atom of central cluster in	Atom's electrons in bonds	Co-valence	Electro-valence	Number of 2e-bonds by sharing	BVS	OS	|*OS*|	IUPAC	CN
H_2O	2	2	0	2	2	−2	2	2	2
H_2O_2	2	2	0	2	2	−1	1	2	2
$HgCl_2$	2	2	0	2	2	+2	2	2	2
Hg_2Cl_2	2	2	0	2	2	+1	1	2	2
SBr_2	2	2	0	2	2	+2	2	2	2
S_2Br_2	2	2	0	2	2	+1	1	2	2
H_2S	2	2	0	2	2	−2	2	2	2
H_2S_2	2	2	0	2	2	−1	1	2	2
CH_4	4	4	0	4	4	−4	4	4	4
C_2H_2	4	4	0	4	4	−1	1	4	2
CrO_3 $^{\text{Fig. 15}}$	6	6	0	6	6	+6	6	6	3
Cr(II) acetate $^{\text{Fig. 15}}$	6	6	0	6	6	+2	2	6	5
$MoCl_6$ $^{\text{Fig. 17}}$	6	6	0	6	6	+6	6	6	6
$MoCl_2$ $^{\text{Fig. 17}}$	6	9	−3	6	9	+2	2	9	9
ReF_7 $^{\text{Fig. 16}}$	7	7	0	7	7	+7	7	7	7
$ReCl_3$ $^{\text{Fig. 16}}$	7	9	−2	7	9	+3	3	9	7
$Ni(CO)_4$ $^{\text{Fig. 18}}$	0	4	−4	0	4	0	0	4	4
$Mn_2(CO)_{10}$ $^{\text{Fig. 19}}$	1	6	−5	1	6	0	0	6	6
$Os_3(CO)_{12}$ $^{\text{Fig. 21}}$	2	6	−4	2	6	0	0	6	6
H_3O^+ conventional	4	3	+1	2	4	−2	2	3	?
H_3O^+ by 8–N rule	2	2	0	2	2	−2	2	2	3
NH_3	3	3	0	3	3	−3	3	3	3
NH_4^+ conventional $^{\text{Fig. 3}}$	5	4	+1	3	5	−3	3	4	?
NH_4^+ by 8–N rule $^{\text{Fig. 4}}$	3	3	0	3	3	−3	3	3	4
BF_4^- conventional $^{\text{Fig. 5}}$	3	4	−1	3	5	+3	3	4	?
BF_4^- 8–N rule $^{\text{Fig. 6}}$	3	3	0	3	3	+3	3	3	4
CO_3^{2-} conventional	4	4	0	4	4	+4	4	4	3
CO_3^{2-} 8–N rule	4	4	0	4	4	+4	4	4	3
C in $\|C{\equiv}O\|$ $^{\text{Fig. 1}}$	2	3	−1	2	3	+2	2	3	1
C in $\|C{=}\overline{\underline{O}}$ 8–N rule $^{\text{Fig. 2}}$	2	2	0	2	2	+2	2	2	1
O in $\|C{\equiv}O\|$ $^{\text{Fig. 1}}$	4	3	+1	2	3	−2	2	3	1
O in $\|C{=}\overline{\underline{O}}$ 8–N rule $^{\text{Fig. 2}}$	2	2	0	2	2	−2	2	2	1
C in $Ni(C{\equiv}O\|)_4$	4	4	0	2	4	+2	2	4	2
C in $Ni(C{=}\overline{\underline{O}})_4$ 8–N rule	4	3	+1	2	3	+2	2	3	2
O in $Ni(C{\equiv}O\|)_4$	4	3	+1	2	3	−2	2	3	1
O in $Ni(C{=}\overline{\underline{O}})_4$ 8–N rule	2	2	0	2	2	−2	2	2	1
KI_3 expand. octet $^{\text{Fig. 22}}$	3	3	0	3	3	−1	1	3	3
KI_3 oct., 8–N rule $^{\text{Fig. 22}}$	1	1	0	1	1	0	0	1	2
N_2	3	3	0	3	3	0	0	3	1
P_4	3	3	0	3	3	0	0	3	3
$\|\overline{\underline{O}}{-}\underline{O}{=}\overline{\underline{O}}\|$	4	3	+1	2	3	+1	1	3	2
O_3 ↑ average reasonance formula	4	3	+1	2	3	+1	1	3	2
$\overline{\underline{O}}{=}\underline{O}{=}\overline{\underline{O}}$ ^{a}	4	4	0	4	4	0	0	4	2
⁝$\overline{\underline{O}}{-}\overline{\underline{O}}{-}\overline{\underline{O}}$⁝ ^{b}	2	2	0	2	2	0	0	2	2
KO_3 paramagnetic, octets	3	2.5	+½	2	2.5	+½	½	?	2

Table 11: (continued)

Unless specified otherwise, central atom or any atom of central cluster in	Atom's electrons in bonds	Co-valence	Electro-valence	Number of 2e-bonds by sharing	BVS	OS	|*OS*|	IUPAC	CN
KO_3 paramagnetic [c]	3	3	0	3	3	0	0	3	?
I in $CsIO_3$ Fig. 7, 8	5	5	0	5	5	+5	5	5	6
O in $AuORb_3$	2	2	0	2	2	−2	2	2	6
$\underline{N}$=N=$\underline{O}$ octets	5	4	+1	3	4	+3	3	4	2
|N≡N–$\overline{\underline{O}}$| octets	5	4	+1	3	4	+2	2	4	2
N_2O ↑ average formula	5	4	+1	3	4	2.5	2.5	4	2
|N≡N=$\overline{\underline{O}}$ after Pauling (Ref. 57 p. 9)	5	5	0	5	5	+2	2	5	2
Au in ClAu[(B⋲)(P⋲)$_2$] Fig. 11	3	4	−1	1	4	+1	1	4	4
B in ClAu[(B⋲)(P⋲)$_2$] Fig. 11	3	4	−1	3	4	+3	3	4	4
Cl in ClAu[(B⋲)(P⋲)$_2$] Fig. 11	1	1	0	1	1	−1	1	1	1
P in ClAu[(B⋲)(P⋲)$_2$] Fig. 11	5	4	+1	3	4	+3	3	4	4

[a] No formal charge, a nonet at central atom. [b] No formal charge, septet at terminal atoms. [c] Nonet at central atom.

9.1 Mn in decacarbonyldimanganese

The $Mn_2(CO)_{10}$ molecule in Fig. 19 illustrates the Mn–Mn bond case listed in Table 11. The bonding follows from the 18-plet rule counted via neutral atoms: Two Mn have 14 valence electrons and 20 obtain from CO molecules. These 34 electrons make 17 pairs on two Mn, hence one pair to be shared. More formally: With $g = 34$ for the $n = 2$ Mn atoms in the generalized 18-plet equation for clusters derived in Section 10.6, $N_{BO} = (18n - g)/2$, yields 1 bonding orbital Mn–Mn. The remaining six electrons on Mn are nonbonding pairs. The same follows from drawing the donated pairs per Mn to get the full Lewis formula (Fig. 20) where the linear bonding of CO to Mn in Fig. 19 implies triple bond in CO.

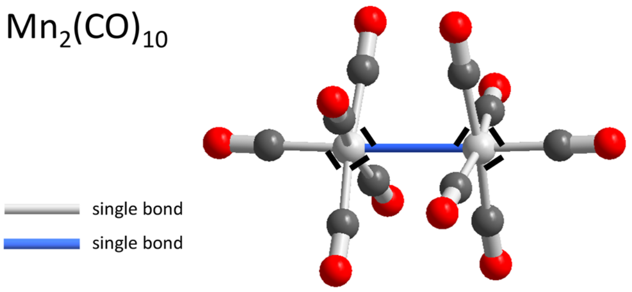

Fig. 19: Molecule of $Mn_2(CO)_{10}$ with lone pairs marked at Mn atoms as black dashes.

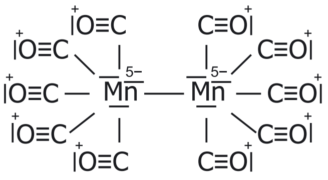

Fig. 20: Lewis formula of $Mn_2(CO)_{10}$ with formal charges.

The Mn atom uses one of its electrons in bonds. In total, it has 6 bonding pairs around. With 6 electrons in nonbonding pairs, the Mn formal charge is 7 − (6 + 6) = −5, compensated by oxygen formal charge +1 on its five ligands in the Lewis formula. Manganese forms 1 homonuclear bond by sharing the remaining "unpaired" electron. The sum of (somewhat idealized) bond valences at Mn is 6.

The oxidation state by Algorithm 1: After assigning bonds to atoms of higher Allen electronegativity and dividing homonuclear bonds equally, Mn is left with 6 electrons in lone pairs and 1 electron from the divided Mn–Mn bond. Its oxidation state is 7 – (6 + 1) = 0. Algorithm 2: The polarity-weighted sum of Mn heteronuclear bond orders gives +5 on the Mn atom of formal charge −5, and 5 – 5 gives again the oxidation state zero.

The present IUPAC definition of valence for Mn "under consideration" evaluates its bonding state by counting F or H it would bond. Such a d^6 Mn, with six two-electron bonds and formal charge −5, would bond like an MnH_6^{5-} giving 6 for this quantity.

9.2 Os in dodecacarbonyltriosmium

Fig. 21 illustrates the Table 11 values for the Os cluster. Counting via neutral atoms, the 24 electrons of 3 Os and 24 electrons donated by CO molecules sum to 48. With $g = 48$ for the $n = 3$ Os atoms in $N_{BO} = (18n - g)/2$ of Section 10.6 yields 3 orbitals bonding the 3 edges of the osmium triangle with 18-plet on each Os.

The Os atom uses 2 of its own electrons in bonds. It has 6 bonding pairs around. With 6 electrons in nonbonding pairs, its formal charge is 8 – (6 + 6) = −4. Each Os forms two homonuclear bonds by sharing own electrons. The sum of bond valences on it is 6.

The oxidation state (Section 4): After assigning bonds to C and dividing homonuclear bonds equally, Os is left with 6 electrons in lone pairs and 2 from the two divided Os–Os bonds. The Os oxidation state is 8 – (6 + 2) = 0. Or, by the second algorithm, the polarity-weighted sum of Os heteronuclear bond orders gives +4 on Os of formal charge −4, and 4 – 4 yields again zero for the oxidation state.

The present IUPAC definition of valence as a quantity for Os "under consideration" follows from its bonding state by counting how many F or H it would bond. Such a d^6 Os, with six two-electron bonds and formal charge −4, would bond like OsH_6^{4-} that yields 6 for this quantity.

9.3 Potassium triiodide

The Lewis formula of the triiodide anion I_3^- is often drawn as single-bonded I–I–I of formal charge −1 at the central iodine. That is not supported by extended-Hückel MO-LCAO calculations from Hoffmann[99] implemented in the program Caesar 2.0,[100] which yield gross ionic charges 0.58– at the terminal iodines and 0.15+ at the central one. In chemical reality, two of those four I–I–I bonding electrons bond the cation to terminal iodines, making the I–I bond order about ½. Such a Lewis formula is in an agreement with the bond lengths in I_3^- of 290 pm[101] versus I_2 of 268 pm.[102] In Fig. 22 of these two alternative formulas, we added the cationic K to visualize the ionic bonding in the 1:1 cation–anion stoichiometry. The valence-type quantity values derived with these two formulas of this salt are in Table 12.

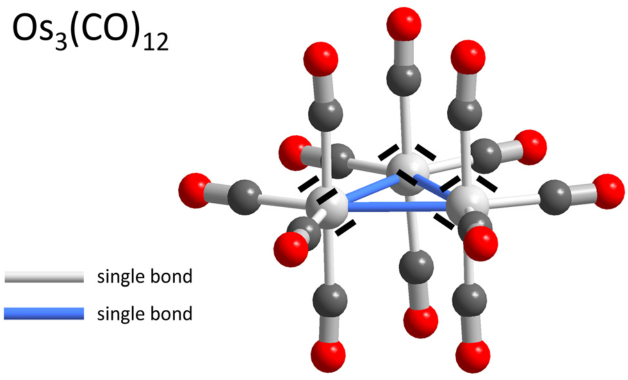

Fig. 21: Molecule of $Os_3(CO)_{12}$ with lone pairs marked at the osmium-cluster atoms.

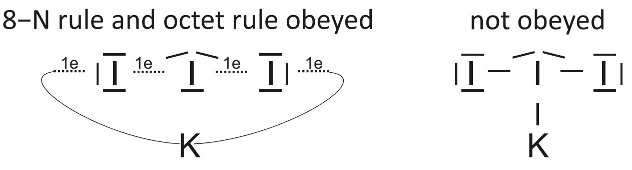

Fig. 22: KI_3 visualized by triiodide Lewis formula respecting the octet and 8−N rule, bonded to K^+ via terminal iodines (left). Lewis formula of expanded octet at the central iodine (right).

Table 12: Quantities tested as definition of valence on Lewis formulas of KI_3 in Fig. 22.

Octet obeyed	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
Central iodine	1	1	0	1	1	0	0	1	2
Terminal iodines	1	1	0	1	1	−1/2	1/2	1	1
K	1	1	0	1	1	+1	1	1	1
Not obeyed	**#e**	**#bp**	**f.c.**	**#p.sh.**	**BVS**	**OS**	**|*OS*|**	**IUPAC**	**CN**
Central iodine	3	3	0	3	3	−1	1	3	3
Terminal iodines	1	1	0	1	1	0	0	1	1
K	1	1	0	1	1	+1	1	1	1

Shorthand symbols of quantity names: #e = number of atom's electrons in bonds; #bp = number of bonding pairs at the atom (co-valence); f.c. = formal charge in the Lewis formula (auxiliary quantity); #p.sh. = number of bonding pairs sharing electrons of both atoms; BVS = bond-valence sum or bond-order sum; OS = oxidation state.

9.4 N_2 and P_4

The current Gold Book [1] IUPAC definition of valence takes one single N atom of 1 lone pair as able to bond three H; valence 3. Only considering, against the spirit of "Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)",[1] the whole |N≡N| molecule as unable to bond Cl or H would yield valence 0 per N equal to its oxidation state. Except for the coordination number, the same valence-type quantities obtain also on the tetrahedron of the P_4 molecule (Table 11).

10 Appendix B: Bond rules for Lewis formulas

Formulations we applied when drawing Lewis formulas of investigated molecules are given in the following. Some reasoning is included.

10.1 The 8−N rule

The eight minus N rule states that an electronegative *sp*-block atom of *N* valence electrons tends to form 8−*N* but not more than four two-electron bonds with atoms of equal or lower electronegativity.[74] In heteroatomic molecules, the rule is enforced by the higher-electronegativity atom, such as fluorine in sulfur fluorides, where bonds in SF_2, SF_4, and SF_6 all keep approximately the single-bond length.[103] [16] In the series BF, CO, and N_2, the triple bond suggested by the octet rule only occurs in N_2, whereas O and F force the bond order towards 2 and 1, respectively.[82]

10.2 The 8+N rule

An electropositive *sp* atom of *N* valence electrons tends to form *N* two-electron ionocovalent bonds with more electronegative atom or atoms.

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[16] Ionic bond of formal charges complying with electronegativity is a two-electron bond too; consider Li–H gradually converting to Li^+ $|H^-$.

10.3 The 18 electron rule

A transition-metal atom in a molecule may tend to surround itself with 18 valence electrons in a bonded state. This is a weaker variant of the noble-gas configuration rule.[104]

10.4 The 12–N (s^2) rule

Atoms down the groups of the periodic system that are close to having 12 *dsp* electrons in their valence shell will tend to lose those that exceed 12 or to gain in bonds those short of 12. The tendency to form s^2 cations is common in the main groups of the periodic system. The tendency to form s^2 anions is specific for Pt and Au that in compounds like Rb_3AuO (Table 11) behave like a relativistic chalcogen and halogen, respectively, as pointed out by Pyykkö.[105]

10.5 The generalized 8–N rule

This rule predicts bonding in a non-metallic and appropriately ionic compound of two *sp*-block elements. In the first step, the valence-electron count VEC_A per the electronegative "anion" atom A is calculated. Excess electrons over 8 remain at the electropositive atom, either as its homonuclear bonds or as lone pairs. Electrons short of 8 are gained by the atom A forming homonuclear bonds. The rule originates in the Zintl concept[106] and its formalized treatments such as in "The General (8–N) rule and its relationship to the Octet rule" by Kjekshus[107] expanded by Parthé.[108]

10.6 The 18-plet rule for transition-metal clusters with ligands

Its derivation starts with the 8–N rule at one single *sp*-block atom; the number of bonding orbitals $N_{BO} = 8 - N$. This converts to the 8–N rule for n cluster atoms in three steps: 8 becomes $8n$, N becomes g (total sum of valence electrons at the cluster, including those donated by ligands[109]), and ½ appears as a factor because each bonding orbital in the "at the atom" 8–N rule now counts for two atoms. That gives $N_{BO} = (8n - g)/2$ valid for *sp* clusters. For transition-metal clusters, the 18 electron rule is adopted; $8n$ becomes $18n$ and $N_{BO} = (18n - g)/2$ listed in "Inorganic structural chemistry"[110] p. 139 for counting outlined already by Sidgwick and Bailey.[109] This formula is used to identify "electron precise" clusters (those bonded by two-electron bonds) of stabilizing 18-plet.

Abbreviations and variables in this text.

The following list explains the meaning or contexts of abbreviations, acronyms, and of variable symbols as used in this report:

CBC	Covalent bond classification
CN	Coordination number of directly bonded atoms
g	Total sum of valence electrons at the cluster
MO-LCAO	Molecular orbitals as linear combinations of atomic orbitals
n	Number of atoms in a cluster, or an integer as a variable in the term n-valent
N or N	Number of valence electrons per atom (N), or in names of 8–N and 18–N rules
N_{BO}	Number of bonding orbitals (here at a cluster)
OS	Oxidation state as a variable in a mathematical expression
sp block	Rectangle of two groups following noble-gas group and six groups ended by it
VEC_A	Valence-electron count per electronegative anionic atom A in a compound

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