

Valence, Oxidation Number, and Formal Charge: Three Related but Fundamentally Different Concepts

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Terms such as “valence” and “oxidation number” appear frequently in both elementary and advanced chemistry texts. However, it is evident from the literature that these terms are often viewed to be synonymous and that conclusions pertaining to such an interpretation may be misleading. The intent of this article is to clarify the notions of valence, oxidation number, and related concepts such as “formal charge” (Table 1), describe their relationship, and comment upon misleading applications.

Valence

Two of the most important factors that provide a first-order evaluation of the nature of a covalent molecule are the electron count (cf. the octet and eighteen-electron rules) and the valence of each atom. However, whereas the term “electron count” is self-evident (i.e., the total number electrons in the valence shell of an atom in a molecule) and used consistently, the word “valence” (also called “valency”) has a plethora of uses, as illustrated by the phrases “valence electrons”, “valence bond theory” (1), “valence shell electron pair repulsion theory (VSEPR)” (2), and “bond-valence model” (3). But when used on its own, to what does valence refer?

The concept of valence, which emerged many years before there existed a detailed understanding of chemical bonding, was originally concerned with a rationalization of molecular composition. In this regard, an understanding of the formulae of simple molecules was once taught by making the analogy that the valence is the number of “hooks” that an atom has to engage with another atom (4). Thus, water has the composition of H₂O because an oxygen atom has a valence of two while a hydrogen atom has a valence of one; as such, the valence of oxygen is satisfied if it bonds to two hydrogen atoms, while the valence of each hydrogen atom is satisfied if it bonds to one oxygen atom (Figure 1). By analogy, ammonia and methane have the compositions NH₃ and CH₄ because the valences of nitrogen and carbon are 3 and 4 respectively (Figure 1). A slightly more complex example is provided by carbon dioxide, for which the formula is CO₂ to satisfy the valence of four for carbon and two for oxygen.

In view of the relationship between the valence of an atom and the molecular formulae of its compounds, the valence of an atom is often described as its “combining power”, a phrase that was first introduced by Frankland with respect to his “atomicity” concept to explain the molecular formulae of zinc, tin, and mercury alkyls (5). Frankland’s atomicity was later named “quantivalence” by Hofmann (1865) and subsequently abbreviated to “valenz” by Kekulé (1867) and Wichelhaus (1868) (5), from which the anglicized forms of valence and valency are derived (6). Sidgwick’s classic 1927 book on *The Electronic Theory of Valency* states that “Valency is a general term used to describe the power which atoms

Table 1. Simple Definitions of Common Terms

Term	Definition
Valence	Number of electrons that an atom uses in bonding.
Oxidation number	The charge remaining on an atom when all ligands are removed heterolytically in their closed form, with the electrons being transferred to the more electronegative partner; homonuclear bonds do not contribute to the oxidation number.
Formal charge	The charge remaining on an atom when all ligands are removed homolytically.
Coordination number	The number of atoms bonded to the atom of interest.

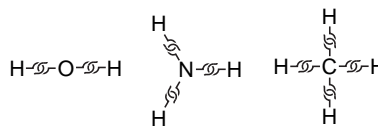


Figure 1. Elementary method for rationalizing molecular formulae in terms of the valence as the number of “hooks” on an atom (the molecules are not drawn with their actual structures to emphasize the notion that the valence was only used to indicate composition).

possess of combining with one another to form molecules” and concludes that “On the whole, the best definition of absolute valency seems to be that adopted by Grimm and Sommerfield, that is, numerically equal to the number of electrons of the atom ‘engaged’ (beansprucht) in attaching the other atoms” (7). While the concepts and definitions of valence have been refined over the years (8), that described by Sidgwick remains the most useful and simple definition for covalent molecules: the valence of an atom in a covalent molecule is simply the number of electrons that an atom has used in bonding.¹ Mathematically, the valence of an atom in a molecule is equal to the difference between (i) the number of valence electrons in the free atom (i.e., the group valence, N) and (ii) the number of nonbonding electrons on the atom in the molecule.

$$\text{valence} = \begin{matrix} \text{number electrons} \\ \text{in valence shell} \\ \text{of free atom} \end{matrix} - \begin{matrix} \text{number non-} \\ \text{bonding electrons} \\ \text{on atom in molecule} \end{matrix} \quad (1)$$

It is, therefore, evident that the determination of the valence of an atom in a molecule requires one to draw an appropriate resonance structure for the molecule and cannot

be determined from an empirical formula alone. The valences of atoms in some simple compounds are illustrated in Table 2.

Employing Sidgwick's preferred definition of valence, it is clear that it is a very important quantity for establishing the properties of a molecule since it indicates how many electrons the atom has used in bonding. As an illustration, if the valence is less than the group valence, it indicates that there are nonbonding electrons on the atom. Such knowledge is important because it provides an indication as to whether or not the atom is capable of using more electrons to form additional bonds. For example, the valence of nitrogen in NH_3 is three, which indicates that there is a pair of electrons on nitrogen that may be used to coordinate additional groups (e.g., BH_3 or H^+). In transition-metal chemistry, knowledge of the number of nonbonding electrons, that is, the d^n configuration, is paramount because it is an important component in determining the magnetic properties and electronic spectroscopy of a molecule. Finally, if the valence of the atom appears to be greater than the group valence, it indicates that either (i) the molecule has been incorrectly formulated or (ii) the bonding cannot be described in terms of 2-center, 2-electron bonds but rather involves 3-center, 2-electron bonds. An example of such a species with 3-center, 2-electron bonds is $(\text{CH}_5)^+$, which is described in more detail below.

As originally employed, the valence of an atom (A) refers to its combining power relative to that of hydrogen; as such, the valence of an atom in a molecule is explicitly and readily indicated by the molecular formula of the hydride AH_n . However, considerable confusion may ensue upon con-

sideration of molecules that are more complex than simple hydrides. For example, valence has been taken to be synonymous with (i) oxidation number (9), (ii) number of bonds (10, 11), and (iii) coordination number (11, 12). The origin of this confusion can be readily seen by consideration of the neutral AH_n hydrides for which the valence, magnitude of the oxidation number, number of bonds, and coordination number each have the same value, n . For example the nitrogen atom in NH_3 has a valence of 3, an oxidation number of -3 , 3 bonds, and a coordination number of 3. In view of the equivalence between valence, magnitude of the oxidation number, number of bonds, and coordination number for simple AH_n hydrides, it is not surprising that these individual concepts have been confused in the literature. However, this relationship for AH_n is purely coincidental and does *not* apply to more complex molecules. A simple illustration of a lack of correspondence between valence, oxidation number, number of bonds, and coordination number is provided by $[\text{NH}_4]^+$. For this species, the nitrogen atom has used all five of its valence electrons (there are no lone pair electrons) and is pentavalent, but its oxidation number is -3 , the number of bonds is 4, and the coordination number is 4. These differences are explained in more detail in the following sections.

Relationship of Valence to Oxidation Number, Number of Bonds, and Coordination Number

As succinctly indicated for $(\text{NH}_4)^+$ above, the valence of nitrogen is not equivalent to either oxidation number, number of bonds, or coordination number. Any such equiva-

Table 2. Comparison of the Valence, Oxidation Number, Number of Bonds, and Coordination Number for Some Simple Molecules

Molecule	No. of Electrons in Valence Shell of Free Atom (N)	No. of Nonbonding Electrons on Atom in Molecule	Valence	Oxidation Number	No. of Bonds	Coordination Number
<i>AH_n: Examples Where Valence = Oxidation Number = No. of Bonds = Coordination Number</i>						
BH_3	3	0	3	+3	3	3
CH_4	4	0	4	-4	4	4
NH_3	5	2	3	-3	3	3
OH_2	6	4	2	-2	2	2
FH	7	6	1	-1	1	1
<i>Examples Where Valence \neq Oxidation Number </i>						
$\text{H}_3\text{C}-\text{CH}_3$	4	0	4	-3	4	4
CMe_4	4	0	4	0	4	4
CH_2Cl_2	4	0	4	0	4	4
$[\text{NH}_4]^+$	5	0	5	-3	4	4
$[\text{OH}_3]^+$	6	2	4	-2	3	3
<i>Examples Where Valence \neq Number of 2-Center, 2-Electron Bonds</i>						
$[\text{BH}_4]^-$	3	0	3	+3	4	4
$[\text{NH}_4]^+$	5	0	5	-3	4	4
<i>Examples Where Valence \neq Coordination Number</i>						
$\text{H}_2\text{C}=\text{CH}_2$	4	0	4	-2	4	3
$\text{HC}\equiv\text{CH}$	4	0	4	-1	4	2
H_3NBH_3	3	0	3	+3	4	4

lence for a given molecule is purely coincidental because a variety of factors cause the relationships to break down, as summarized in Table 3 and described in more detail below.

Valence and Oxidation Number

The oxidation number of an atom in a molecule is based on a formalism that forces a covalent compound to possess complete *ionic* character and may be defined as the charge that an atom would have if all bonds to it are broken such that the ligands retain a closed-shell configuration (Figure 2); an exception, however, refers to homonuclear bonds, in which case the bond is broken homolytically and a single electron is transferred to each atom (13). The oxidation number may thus simply be expressed as

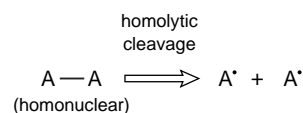
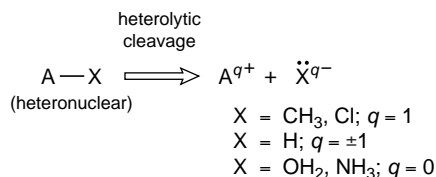
$$\text{oxidation number} = \text{charge on compound} - \text{charge on ligands} \quad (2)$$

In many cases, the charges assigned to simple monoatomic ligands do not vary from compound to compound, as illustrated by F^- , Cl^- , and O^{2-} . However, a notable exception is provided by hydrogen for which both H^+ and H^- have permissible closed-shell configurations ($1s^0$ and $1s^2$, respectively). In this case, the charge assigned to hydrogen is determined by the relative electronegativity of the atom to which it is attached.

As will be discussed in more detail below, it is important to emphasize that the derived charge does *not* correspond to the charge on the atom in the molecule, but is *hypothetical*. In this regard, it is unfortunate that the oxidation number is often described as a “formal charge” because this term has a very distinct and different meaning to that of oxidation number (*vide infra*) (14).

In many situations, the valence of an atom in a molecule may be coincidentally equal to its oxidation number. However, examination of Tables 2 and 3 demonstrates that there are several factors that cause this relationship to break down. Specifically, valence and oxidation number are not the same when either (i) homonuclear element–element bonds are present, (ii) the ligands attached to the atom of interest

fragmentation method for assigning oxidation numbers (exaggerates ionic character)



fragmentation method for assigning formal charges (exaggerates covalent character)

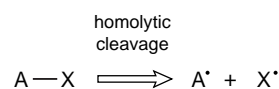


Figure 2. Fragmentation methods for assigning oxidation number and formal charge.

The fragmentation method for assigning oxidation numbers exaggerates the ionic component of the bond and involves the conceptual *heterolytic cleavage* of the A–X bond such that the pair of electrons is transferred to the more electronegative atom; an exception is for homonuclear bonds that are cleaved homolytically.

In contrast, the fragmentation method for assigning formal charges exaggerates the covalent character and involves the *homolytic cleavage* of the A–X bond such that each atom receives a single electron.

Table 3. Situations Where the Equivalence of Valence to the Magnitude of Oxidation Number, Number of Bonds, and Coordination Number Break Down

Parameter	Factors That Cause the Break Down	Examples
Oxidation number	(i) homonuclear element–element bonds are present	(i) Me_4C : C is tetravalent but has an oxidation number of zero.
	(ii) two ligands attached to the atom of interest have opposite charges (e.g., Cl^- and H^+)	(ii) CH_2Cl_2 : C is tetravalent but has an oxidation number of zero.
	(iii) the molecule is charged and the ligand is dissociated as a cation (e.g., H^+)	(iii) $[NH_4]^+$: N is pentavalent but has an oxidation number of -3.
No. of bonds	the atom in question bears a formal charge (valence = no. of bonds + formal charge)	$[BH_4]^-$: B is trivalent but has four bonds. $[NH_4]^+$: N is pentavalent but has four bonds.
Coordination number	(i) a multiple bond is present	(i) $H_2C=CH_2$: C is tetravalent but 3-coordinate $HC\equiv CH$: C is tetravalent but 2-coordinate.
	(ii) a dative ligand is present	(ii) H_3NBH_3 : B is trivalent but 4-coordinate

NOTE: This table is only intended to demonstrate examples of situations in which the equivalence breaks down; it is not intended to be a comprehensive list.

are dissociated with opposite charges, for example, H^+ and Cl^- , or (iii) the molecule is charged and the ligand is dissociated as a cation, for example, H^+ (16). For example, (i) the valence of the central carbon in CMe_4 is four, but the oxidation number is zero because homonuclear element–element bonds are neglected in the determination of oxidation number; (ii) the valence of carbon in CH_2Cl_2 is four, but the oxidation number is zero because, in terms of electronegativity differences with respect to carbon, H is viewed as “ H^+ ” and Cl is viewed as “ Cl^- ”; and (iii) the valence of nitrogen in $(\text{NH}_4)^+$ is five, but its oxidation number is -3 .

Valence and Number of Bonds

The equivalence between valence and number of 2-center, 2-electron bonds for molecules of the type AH_n breaks down when the atom in question bears a formal charge (vide infra). For example, consider the series of isoelectronic molecules $(\text{BH}_4)^-$, CH_4 , and $(\text{NH}_4)^+$; while each of the molecules exhibits four bonds to the central atom, the valences of boron, carbon, and nitrogen are 3, 4, and 5, respectively. In this regard, it is pertinent to note that there exists a simple relationship between valence and the number of bonds, namely

$$\text{valence} = \frac{\text{number of bonds}}{\text{of bonds}} + \text{formal charge} \quad (3)$$

As such, it is evident that, for neutral molecules of the type AH_n , the coincidental equivalence between valence and number of bonds is a consequence of the central atom bearing no formal charge.

Valence and Coordination Number

The coordination number is simply defined as the number of atoms attached to the atom of interest in a molecule (15). For molecules of the type AH_n the coordination number of A, n , is equivalent to its valence. However, the equivalence between valence and coordination number breaks down when a multiple bond is present. For example, consider the series of molecules: $\text{H}_3\text{C}-\text{CH}_3$, $\text{H}_2\text{C}=\text{CH}_2$, and $\text{HC}\equiv\text{CH}$. The valence of carbon in each molecule is four, but the coordination numbers are 4, 3, and 2, respectively. In essence, when the central atom uses more than one of its electrons to bond to another atom, the coordination number of the central atom is reduced from the value of its valence.

Likewise, the relationship between valence and coordination number breaks down when the bond is a *dative* covalent bond (also referred to as coordinate covalent bond or donor–acceptor bond) (16). As the name implies, in a dative covalent bond, one of the atoms provides *both* electrons. Examples of ligands that coordinate in this manner are those with lone pairs, for example, H_2O and NH_3 . Coordination of one of these dative ligands to an atom A does not require any electrons from A and thus the valence of A does not change upon coordination of the ligand. For example, the valence of boron in three-coordinate BH_3 is three and it remains three upon coordination of NH_3 , even though its coordination number increases to four (Figure 3). From the opposite perspective, it is evident that the valence of the coordinating atom of a dative ligand increases by *two* units when it coordinates to a Lewis acidic site. Thus, while the nitrogen in NH_3 is trivalent, it becomes pentavalent once it uses its lone pair upon coordinating to a Lewis acid (e.g., BH_3 or H^+).

Comparison of the Use of Valence and Oxidation Number To Provide Insight into the Nature of a Molecule

While valence has inadvertently been taken to be synonymous with (i) oxidation number, (ii) number of bonds, and (iii) coordination number, by far the greatest confusion is with oxidation number. Notwithstanding this confusion, which will be addressed in more detail below, it is pertinent to consider whether it is the valence or oxidation number that provides the greater insight into understanding the nature of a molecule. To address this issue, the oxidation numbers and valences of carbon in some simple organic molecules are listed in Table 4, of which several points should be noted.

Firstly, the oxidation numbers of carbon span the substantial range of -4 to $+4$. For example, the oxidation number of carbon in CH_4 is -4 , whereas that in CCl_4 is $+4$ (recall that hydrogen is treated as “ H^+ ” because it is more electropositive than carbon, while chlorine is treated as “ Cl^- ” because it is more electronegative than carbon). The 8 units of variation of oxidation number between CH_4 and CCl_4 is most

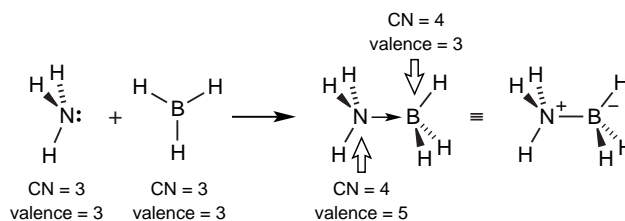


Figure 3. Illustration of how the valence and coordination number (CN) varies upon the formation of a dative covalent bond, which may be represented as an “arrow” or its equivalent from with a “line” and formal charges. The coordination number of both the donor (NH_3) and acceptor (BH_3) increase by one unit upon formation of the adduct, the valence of the boron does not change (because it uses no electrons in forming the bond) and the valence of nitrogen increases by two units (because it uses two electrons in forming the dative bond).

Table 4. Comparison of Valence and Oxidation Numbers of Carbon in Simple Organic Compounds

Compound	Oxidation Number	Valence
CH_4	-4	4
CH_3Cl	-2	4
CH_2Cl_2	0	4
CHCl_3	$+2$	4
CCl_4	$+4$	4
Me_4C	0	4
Me_2CCl_2	$+2$	4
$(:\text{CCl}_2)$	$+2$	2
MeCH_3	-3	4
(CH_3^\bullet)	-3	3
CH_3OH	-2	4
MeCH_2OH	-1	4
$\text{Me}_2\text{C}(\text{H})\text{OH}$	0	4
Me_3COH	$+1$	4

impressive, but does the difference in the nature of CH_4 and CCl_4 warrant such a large change in oxidation number? For example, CH_4 (with the most negative oxidation state) is not a widely used reducing agent, and CCl_4 (with the most positive oxidation state) is not a widely used oxidizing agent. Correspondingly, CH_2Cl_2 is not conventionally regarded as either an oxidizing agent or a reducing agent, even though the carbon possesses an oxidation number of zero. Me_4C is also an example of a compound that contains carbon in the zero oxidation state, but its chemistry has little in common with that of CH_2Cl_2 . As such, the large variation in oxidation number cannot be regarded as providing much insight into the nature of these molecules.

A further illustration of how oxidation number may offer little insight into the chemistry of a molecule is provided by the fact that both Me_2CCl_2 and $(:\text{CCl}_2)$ have an oxidation number of +2, but the chemistry of these molecules are *very* distinct. Thus, whereas Me_2CCl_2 is a stable species, the carbene $(:\text{CCl}_2)$ is only known to exist as a reactive intermediate (17). Likewise, the carbon atoms in both CH_3CH_3 and CH_3^\bullet have an oxidation number of -3, but the former compound is a stable molecule while the latter is a highly reactive radical.

While examination of the compounds listed in Table 4 clearly indicates that the oxidation number per se provides no indication of compound stability or reactivity, it is evident that the valence of an atom in a molecule *does* provide useful information. Thus, with two exceptions, all of the compounds listed in Table 4 exhibit a valence of 4 for carbon, despite the fact that the oxidation numbers range from +4 to -4. The two exceptions are $(:\text{CCl}_2)$, with a valence of 2, and (CH_3^\bullet) with a valence of 3. These exceptions are notable because they correspond to the two compounds in Table 4 that are not isolable under normal conditions. The valence of an atom in a molecule, therefore, provides a much more meaningful criterion for evaluating the chemical reasonableness of a molecule than does the oxidation number. Thus, while the concept of oxidation numbers is of use in certain situations, such as the balancing of redox equations, it is less fundamental than the underlying concept of valence and its use in evaluating the chemical reasonableness of a molecule is only successful when the oxidation number and valence of an atom in a molecule are coincidentally the same.

Other inadequacies arising from the assignment of oxidation numbers to simple organic compounds have also been noted (18). For example, the oxidation number of the α -carbon atom in a series of alcohols is -2 for $\underline{\text{C}}\text{H}_3\text{OH}$, -1 for $\text{Me}\underline{\text{C}}\text{H}_2\text{OH}$, 0 for $\text{Me}_2\underline{\text{C}}(\text{H})\text{OH}$, and +1 for $\text{Me}_3\underline{\text{C}}\text{OH}$. While it was recognized that it is unreasonable for the oxidation number of the α -carbon atom to vary by 3 units in such a series of alcohols, the proposed solution to the problem was merely to assign a charge of zero to hydrogen atoms when attached to carbon (18)! Although it is true that such a procedure would result in the oxidation number of the α -carbon in each alcohol being the same (+1), the hydrogen atom H^\bullet is *not* a closed-shell species and the assignment of zero charge is totally inappropriate for the determination of oxidation numbers (as noted above, the permissible forms for hydrogen are H^+ and H^- with closed-shell configurations of $1s^0$ and $1s^2$, respectively). The desire to change the rules for determining oxidation numbers on a case-by-case basis is

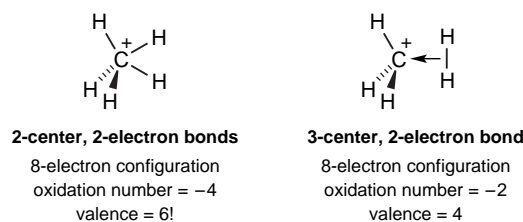


Figure 4. 3-Center, 2-electron bonding in $(\text{CH}_5)^+$.

an illustration of the failing of the use of oxidation numbers in providing insight into the nature of a compound. Examination of Table 4, however, indicates that each of the alcohols possess carbon in the same valence state and thereby reiterates the ability of valence to provide a greater appreciation of chemical reasonableness than does oxidation number.

Knowledge of the valence of an atom in a molecule is important because it provides the fundamental information as to *how many of its electrons have been used in bonding*. This information is essential because it allows one to ascertain (i) whether the atom has enough electrons to support the number of atoms attached via 2-center, 2-electron bonds and (ii) whether any electrons remain on the atom and are available for subsequent reactivity.

As an illustration of the first point, consider the molecule $(\text{CH}_5)^+$ (Figure 4). On the basis of its oxidation number (-4) and octet configuration, the molecule would appear to be perfectly reasonable; indeed, the carbon atom in $(\text{CH}_5)^+$ has the same oxidation number and electronic configuration to that of CH_4 . However, the valence of carbon in $(\text{CH}_5)^+$ provides a clear indication that there is something unusual about such a molecule. Specifically, the valence of carbon in $(\text{CH}_5)^+$ would be 6 (see eq 3), but carbon only has 4 valence electrons! Thus, while both the oxidation number and octet configuration provide no indication that there is anything unusual about $(\text{CH}_5)^+$, the implausible valence state of carbon immediately calls into question the nature of this species. Indeed, $(\text{CH}_5)^+$ is very unstable, but is sufficiently stable to be generated by protonation of methane in superacidic media (12). But how could such a species exist if the valence of carbon were to be 6? Since the carbon atom in CH_4 does not have any electrons available for protonation (unlike the nitrogen atom in NH_3), the answer is quite simply provided by the fact that it is *not* the carbon atom itself that is protonated. Rather, it is the C-H *bond* that is protonated, thereby resulting in a 3-center, 2-electron interaction (Figure 4) (19). With a 3-center, 2-electron interaction, $(\text{CH}_5)^+$ may be regarded as a dihydrogen complex of $(\text{CH}_3)^+$, that is, $[\text{H}_3\text{C}(\eta^2\text{-H}_2)]^+$, and so the valence of the carbon in this species remains 4 (20). Thus, because it is the C-H bond that is protonated, the carbon atom in “ $(\text{CH}_5)^+$ ” contributes only 4 valence electrons to bonding the 5 hydrogen atoms.

An illustration of the second point, that is, the use of valence to provide an indication of whether there are any electrons available on the atom for further bonding, is provided by consideration of NH_3 . Thus, the valence of nitrogen in NH_3 is three, thereby indicating that there is a pair of electrons available for subsequent reactivity, such as protonation or coordination to a Lewis acid.

Valence and Oxidation Number: Examples of Misleading Applications

The above discussion has emphasized how oxidation number is not synonymous with valence and that it is the latter concept that is the more useful when it comes to evaluating the nature of a molecule. Using oxidation number in place of valence may give a misleading description of a molecule, as illustrated by the classification of whether or not a molecule is “subvalent”, that is, one in which the valence of an atom in a compound is less than the group valence.

For example, the appropriate distinction between valence and oxidation state is often not made when discussing the chemistry of mercury(I) compounds of empirical formula HgX (e.g., $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$). These compounds have been described as representing a deviation from the divalent state; (21) however, while such complexes are appropriately characterized as mercury(I) derivatives, it is inappropriate to describe the mercury in these compounds as univalent because the compounds are *not* composed of discrete monomeric HgX species but are actually dinuclear with a $\text{Hg}-\text{Hg}$ bond. Thus, while an isolated HgX molecule (or Hg^+ ion) possesses univalent mercury with an unpaired electron, this electron is used in forming the $\text{Hg}-\text{Hg}$ bond and the mercury becomes divalent in mercury(I) Hg_2X_2 compounds (Figure 5).

The *interesting* distinction between Hg(I) and Hg(II) compounds is not so much concerned with the change in oxidation number, but is rather concerned with the fact that the former compounds possess a $\text{Hg}-\text{Hg}$ bond. In this regard, the chemistry of mercury is quite distinct from that of its lighter congeners (zinc and cadmium), which show little propensity to form complexes with $\text{M}-\text{M}$ bonds. Indeed, the first example of a complex with a $\text{Zn}-\text{Zn}$ bond, Cp^*_2Zn_2 , where Cp^* is C_5Me_5 , has only recently been reported (22).

While mercury(I) compounds of the type Hg_2X_2 should not be categorized as subvalent, *bona fide* subvalent com-



Figure 5. Distinction between oxidation number and valence in Hg_2X_2 compounds.

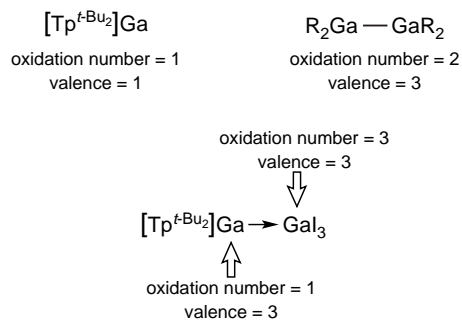


Figure 6. Differences between oxidation number and valence of gallium in compounds with Ga–Ga bonds: $\text{Tp}^{\text{t-Bu}_2}$ is tris(3,5-di-*t*-butylpyrazolyl)hydroborato and R is $(\text{Me}_3\text{Si})_2\text{CH}$.

pounds are known for the adjacent group 13 elements. Indeed, the subvalent ($N - 2$) state is so well precedented for these elements that the phenomenon is often described in terms of the “inert-pair” effect (23). However, the tendency to form subvalent compounds diminishes quite rapidly upon ascending the periodic table. Thus, whereas monovalent complexes of thallium and indium are well known (e.g., InCl and TlCl), such derivatives of the lighter group 13 elements (B, Al, Ga) are extremely rare (24) and the first discrete (i.e., not mixed-valent) monovalent gallium complex to be structurally characterized by X-ray diffraction, namely the *tris*(pyrazolyl)borate complex $(\text{Tp}^{\text{t-Bu}_2})\text{Ga}$ was only reported in 1996 (25). However, with respect to the aforementioned issue of metal–metal bonds causing the oxidation number to be reduced from the value of the valence, it is appropriate to point out that there are many examples of gallium complexes in which the oxidation number is less than +3, but these typically possess Ga–Ga bonds and so are actually trivalent gallium compounds, for example, $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Ga}\}_2$ (Figure 6) (26, 27). Furthermore, although the hypothetical molecule $\text{H}_2\text{Al}-\text{AlH}_2$ has been described as divalent (26), as has $\text{LBr}_2\text{Al}-\text{AlBr}_2\text{L}$ ($\text{L} = \text{anisole}$) (29, 24c), they are more appropriately described as trivalent.

Another interesting example of how the oxidation number and valence are not the same in the presence of a metal–metal bond is provided by the molecule $(\text{Tp}^{\text{t-Bu}_2})\text{GaGaI}_3$, which may be regarded as an adduct between monovalent $(\text{Tp}^{\text{t-Bu}_2})\text{Ga}$ and trivalent GaI_3 (Figure 6). In view of the latter description, it would be tempting to view $(\text{Tp}^{\text{t-Bu}_2})\text{GaGaI}_3$ as a mixed-valent derivative comprised of monovalent and trivalent gallium centers. However, this viewpoint would be incorrect because the gallium of the $[(\text{Tp}^{\text{t-Bu}_2})\text{Ga}]$ moiety in $(\text{Tp}^{\text{t-Bu}_2})\text{GaGaI}_3$ is actually *trivalent* because the pair of electrons that are available in mononuclear $(\text{Tp}^{\text{t-Bu}_2})\text{Ga}$ are used to coordinate the GaI_3 fragment. Thus, the gallium uses all three of its valence electrons in forming $(\text{Tp}^{\text{t-Bu}_2})\text{GaGaI}_3$ and so is trivalent. Despite the fact that both gallium centers in $(\text{Tp}^{\text{t-Bu}_2})\text{GaGaI}_3$ are trivalent, the oxidation numbers are +1 and +3. The distinction is significant because the +1 oxidation state could be taken to imply that the gallium center still has a pair of electrons available for bonding, but this is not the case.

Although the above examples have focused on compounds of the main-group metals, it is important to note that many similar problems are encountered in transition metal chemistry. For example, $\text{Mn}_2(\text{CO})_{10}$ is a compound of manganese in the zero oxidation state, which may therefore be taken to imply an unusual d^7 configuration. However, $\text{Mn}_2(\text{CO})_{10}$ possesses a $\text{Mn}-\text{Mn}$ bond derived by interaction of the unpaired electrons of two $(\text{CO})_5\text{Mn}^{\bullet}$ radicals and so the manganese in this complex is monovalent; as such, the manganese actually has the much more common d^6 configuration.

Comparison of Oxidation Number, Formal Charge, and “Actual” Charge

Finally, before concluding this article it is pertinent to note that the oxidation number formalism is only one of the methods of assigning a charge to an atom in a molecule. A second type of charge that may be assigned to an atom in a

molecule is the “formal charge” (FC). The formal charge of an atom in a given Lewis structure is the charge it would possess if the electrons in each covalent bond were to be distributed equally between the two bonded atoms such that each partner receives one electron (29). The formal charge may, therefore, be defined as the difference between (i) the number of electrons in the free atom (i.e., the group valence) and (ii) the number of electrons remaining on the atom in a molecule when all bonds are broken homolytically (30).

$$\text{formal charge} = \begin{array}{l} \text{number electrons} \\ \text{in valence shell} \\ \text{of free atom} \end{array} - \begin{array}{l} \text{number electrons} \\ \text{remaining on atom in} \\ \text{molecule after all bonds} \\ \text{are broken homolytically} \end{array} \quad (4)$$

Since each 2-center, 2-electron bond contributes one electron to the electron count of an atom in a molecule, the electron count is equal to the number of electrons in the valence shell of the *free* atom plus the number of covalent bonds, adjusted by the formal charge. Thus, the formal charge may also be expressed as:

$$\text{formal charge} = \begin{array}{l} \text{number electrons} \\ \text{in valence shell} \\ \text{of free atom} \end{array} + \begin{array}{l} \text{number of} \\ \text{bonds} \end{array} - \begin{array}{l} \text{electron} \\ \text{count} \end{array} \quad (5)$$

For example, for a series of isoelectronic $(\text{XH}_4)^q$ ($X = \text{B}, \text{C}, \text{N}$; $q = -1, 0, +1$) molecules with an octet configuration, the formal charges on the central atoms are -1, 0, and +1, respectively (Table 5).

While the concepts of oxidation number and formal charge are closely related in the sense that they both refer to a charge on an atom in a molecule, they have very different values because the charges are determined by two fundamentally different formalisms that respectively exaggerate the *ionic* and *covalent* character of the bonding (Figure 2).³ Far too frequently in the literature, these quantities are implied to be related to the “actual” charge on the atom in question. However, since the oxidation number and formal charge have very different values, it is evident that it is not possible for them both to be used in this way. A fundamental question, therefore, is does the “actual” charge on an atom in a covalent molecule correspond more closely to the oxidation number or the formal charge? To answer this question, the oxidation numbers and formal charges for some simple molecules are compared with the calculated charges obtained by theoretical methods in Table 6 (31). Not surprisingly, in each case, the calculated charges have values that are intermediate between the formal charge and oxidation number (32). For the examples listed in Table 6, the calculated charges are closer in magnitude to the formal charge than the oxidation number, but the *sign* of the calculated charge may often be different to that of the formal charge. For example, consider the nitrogen atom in $(\text{NH}_4)^+$ with a formal charge of +1, an oxidation number of -3 and a calculated charge of -0.84 (33); the calculated charge is closer to the formal charge than the oxidation number, but is of an opposite sign. Therefore, it is evident that neither oxidation number nor formal charge should be regarded as an indication of a charge in a molecule.

In this regard, it is worth noting that charge on an atom is typically considered to be less than $|\pm 1|$, a concept that is known as the Pauling electroneutrality principle (34). For example, discussing the oxidation number of iron in $(\text{FeO}_4)^{2-}$

and $[\text{Fe}(\text{CO})_4]^{2-}$, Roald Hoffmann writes: “Is there really a charge of +6 on the iron in the first compound, and a -2 charge in the carbonylate? Of course not, as Pauling told us in one of his many correct (among some incorrect) intuitions. Such large charge separation in a molecule is unnatural. Those ions aren't bare—the metal center is surrounded by more or less tightly bound ‘ligands’ of other simple ions (Cl^- for instance) or molecular groupings (CN^- , H_2O , PH_3 , CO). The surrounding ligands act as sources or sinks of electrons, partly neutralizing the formal charge of the central metal atom. At the end, the net charge on a metal ion, regardless of its oxidation state, rarely lies outside the limits of +1 to -1” (35).

Of the two classes of artificial charges associated with atoms in molecules, many inorganic chemists tend to focus more on the oxidation number as being of greater significance in determining the chemical properties of a molecule. In large part this is a consequence of the fact that in many examples the oxidation number is *coincidentally* the same as the valence of the atom and is *not* a result of the charge associated with the atom.

Formal charges are useful for electron bookkeeping purposes and for suggesting which resonance structure may be the best description for the structure of a molecule. For example, it is often taught that (i) structures with negative formal charges on electronegative elements are favored, (ii) structures that minimize the number of formal charges are favored (36), and (iii) structures with the same sign charge on adjacent atoms are disfavored. In this regard, it is important to emphasize that, in contrast to oxidation number, the formal charge of an atom in a molecule depends on the resonance structure that is being considered. For example, the formal charge on osmium in OsO_4 is zero if the osmium-

Table 5. Calculation of Formal Charges for $(\text{XH}_4)^q$ ($X = \text{B}, \text{C}, \text{N}$; $q = -1, 0, +1$)

Element	No. of Electrons in Valence Shell of Free Atom	No. Electrons Remaining on the Atom when Bonds Are Broken Homolytically	Formal Charge
B	3	4	-1
C	4	4	0
N	5	4	+1

NOTE: Formal charge is the number of electrons in the valence shell of the free atom - number of electrons remaining on the atom in a molecule when all bonds are broken homolytically.

Table 6. Comparison of Oxidation Number, Formal Charge, and Calculated Charge for Some Simple Molecules

Molecule	Oxidation Number	Calculated Charge ^a	Formal Charge
CH_4	-4	-0.82	0
$(\text{CH}_3)^+$	-2	0.35	+1
$(\text{CH}_3)^-$	-4	-1.36	-1
NH_3	-3	-1.05	0
NH_4^+	-3	-0.84	+1

^aData calculated using NBO/6-311G**++

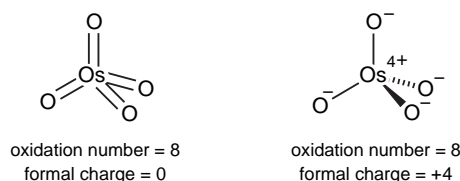


Figure 7. Illustration of how formal charge depends on resonance structure, whereas oxidation number is independent.

oxygen bond is represented as a $\text{Os}=\text{O}$ double bond, but is +4 if the bond is represented as Os^+-O^- ; in each case, however, the oxidation number is +8 because the oxygen is removed as a “-2” ligand regardless of the precise nature of the bonding interaction (Figure 7).

Summary

Two of the most important factors that provide a first-order evaluation of the nature of a covalent molecule are the electron count and the valence of each atom. Of these, the valence of an atom in a molecule is highly significant because it describes how many of the atom's electrons have been utilized in bonding. Perusal of the literature, however, indicates that valence is frequently taken to be synonymous with oxidation number, coordination number, and number of bonds. Unfortunately, this equivalence only exists for simple neutral molecules of the type AH_n and breaks down in many circumstances (Tables 2 and 3). For example, the presence of a homonuclear A–A bond causes the valence to deviate from the oxidation number and in such situations the use of oxidation number instead of valence can result in misleading descriptions of molecules. The terms valence, oxidation number, coordination number, and number of bonds each have individual meanings and it is neither wise nor appropriate to use them interchangeably.

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Notes

1. It is pertinent to note that additional terms such as covalency and electrovalency (or ionic valency) have also been used (7). The former refers to the formation of a covalent bond, while the latter refers to complete electron transfer to form ions, with “positive electrovalency” being used to express the number of electrons released by an element, while “negative electrovalency” describes the number of electrons added. The total valence is the sum of the covalency and electrovalency and it can be readily seen that this is equivalent to the simple expression: valence = no. of covalent bonds + formal charge.

2. Discrepancies between valence and oxidation number also arise when the ligands are proposed to have cationic closed-shell configurations, for example, NO^+ and $(\eta^7-\text{C}_7\text{H}_7)^+$. A consideration of these issues is beyond the scope of this article.

3. Note that the definition of formal charge (eq 4) can be readily modified to give an expression for its counterpart, oxidation number (ON), that is, $\text{ON} = \text{no. electrons in valence shell of free atom} - \text{no. electrons remaining on the atom in a molecule when all bonds are broken heterolytically}$.

Note Added in Proof

For a relevant article that was published after acceptance of this article, see Smith, D. W. *J. Chem. Educ.* **2005**, *82*, 1202–1204.

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- In fact, the term “valence number” was replaced by “oxidation number” because of the misleading association with “valence”. For example, Glasstone commented “The ‘valence numbers’ (now read ‘oxidation numbers’) of C in oxalic acid, formic acid and formaldehyde are +3, +2, and 0, respectively, yet there is no question concerning the quadrivalence of carbon in these compounds.” See Glasstone, S. *J. Chem. Educ.* **1948**, *25*, 278–279.
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