3.4

ON THE DISTINCTIONS BETWEEN THE CONCEPTS OF ELECTROVALENCY AND OF OXIDATION NUMBER

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VALENCY OF AN ELEMENT

THE valency w of a *metalloid element* is the number of electrons missing from its atom compared with the structure of the rare gas that follows it. This valency is always unique. Examples: $w_S = 2$; $w_N = 3$, etc.

The valency w of a *metallic element* is the number of electrons which the atom possesses in excess of a more or less stable structure.

For the *fundamental metals*, the shell immediately underlying the valency electrons is the very stable one of the preceding rare gas. The valency is again unique. Examples: $w_K = 1$; $w_{Ca} = 2$, etc.

For the *transition metals*, the shell immediately underlying is richer in electrons than that of the preceding rare gas. There are several valencies, determined not only by the excess electrons relative to the shell immediately underlying, but also by the electrons that can be lost from that shell by the usual chemical operations.

For the *transition metals preceding the triads*, the *maximum valency* w_M corresponds to the number of excess electrons relative to the structure of the preceding rare gas. Examples: $w_M = 6$ for Cr.

For the *transition metals following the triads*, the *maximum valency* w_M is usually equal to the number of excess electrons relative to the immediately underlying shell that contains 18 electrons, of the so-called *pseudo-rare gas*. Example $w_M = 2$ for Zn. Exceptions to this rule are the more probable when the metals considered are next to the triads. Examples: $w = 1$ or 2 for Cu, Ag whilst the rule predicts $w_M = 1$.

Amphoteric elements may be defined as those in which the atoms can acquire a stable structure by losing or gaining an equal number of electrons. Their valency is thus the same in either case. This occurs, for example, on the one hand with hydrogen ($w = 1$) which on acquiring an electron changes to the structure of helium, and on losing an electron changes to the structure of the neutron which may be regarded as a rare gas of atomic number zero; and on the other hand, with the elements (C, Si, Ge, Sn, Pb, for which $w = 4$) possessing four external electrons in which the immediately underlying structure is that of a rare gas or of a pseudo-rare gas.

ELECTROVALENCY OF A GROUP

The *electrovalency* z of a simple or compound group is the charge, positive or negative, of this group expressed in electrons. According to the

recommendation of the 'Commission on the reform of inorganic nomenclature of the I.U.P.A.C.', an ion is symbolized by allotting to the corresponding chemical symbol the exponent z. Examples: Mg^{+2}, N^{-3}, SO_4^{-2}, etc. . . . except that the absolute value is omitted when $z = \pm 1$. Examples: K^+, NO_3^- etc.

By extension, $z = 0$ for a *neutral group* and in certain cases, it is convenient to indicate such an exponent. Examples: Cu^0, I^0, etc.

For *free ions in solution* (not considering their actual solvation) the electrovalency is obtained experimentally by electrochemical means. For a simple ion, its numerical magnitude is the same as the valency (or one of the valencies) of the corresponding element. Examples: for Cl, $w = 1$; for Cl^-, $z = -1$, $|z| = 1$. For Fe, $w_1 = 2$, $w_2 = 3$, . . .; for Fe^{2+}, $z = 2$; for Fe^{3+}, $z = 3$.

For *free gaseous ions*, the electrovalency can be obtained experimentally by mass spectrography. If it is for a simple ion, its numerical magnitude is not necessarily equal to the valency of the corresponding element. Example: for He, $w = 0$; for He^{+2} (α-particle), $z = +2$.

For *simple combined ions* (in solution or gaseous), that is, the interiors of complex groups, there is no general method in existence for determining the electrovalency experimentally. Each hypothesis should have a theoretical basis consistent with the observed facts. The electrovalency of a combined ion is not necessarily equal to the electrovalency of a free ion (assuming that the latter is one that is known) of the same element. For example, from the fact that water is dissociated into H^+ and OH^- it cannot be concluded that the hydrogen is already in the state H^+ in the water molecule, because this also dissociates into H and OH (according to spectroscopic evidence) at high temperature. The electrovalency of a combined ion varies also, in principle, depending upon the compound considered. For example, if the electrolytic properties of solutions of HCl are inferred from the presence of an H^+ compound in the gaseous molecule, then the electrolytic properties of molten LiH which exhibits free H^-, contradict the presence of combined H^+ in crystalline LiH.

However, the electrovalency of a *combined ion in solution* cannot have any magnitude whatsoever. In *the case of a metalloid* it is subject to the double inequality $-w \leqslant z \leqslant 8 - w$, in which the two extreme terms represent the respective stabilities of the rare gas that follows and the rare or pseudo-rare gas that precedes. For example, the electrovalency of sulphur ions ($w = 2$) certainly lies between -2 and $+6$. In *the case of a metal* it is usually agreed that the minimum electrovalency is zero, whilst the maximum electrovalency z_M coincides with its maximum valency w_M. For example, the electrovalency of manganese ions ($w_M = 7$) lies between 0 and 7.

The numerical magnitude of the electrovalency of a combined ion does not express the number of monoelectrovalent ions of opposite sign by which this ion can surround itself in a dissolved complex form or in a crystalline structure. This number which defines the co-ordination number i corresponds, if the bonds are due to electrostatic attractions, to the configuration of minimum potential energy compatible with the space occupied by the groups concerned. At every other temperature except the absolute zero, the kinetic energy must be taken into account, according to KOSSEL[1]. For

example, $i=8$ in the crystals of CsCl; $i=6$ in the AlF^{-3} ion in solution, whilst $z_{Al^{+3}} = +3$.

COVALENCY OF A SIMPLE GROUP

The covalency of a simple group is the number v (always positive) of electrons that it is necessary to link with it in order to give it an effective stability.

In the *case of a metalloid*, this stability corresponds to the structure of the rare gas that follows it. Examples: $v_{Cl}=1$; $v_{Cl^-}=0$; $v_{Cl^+}=2$, etc.

In the *case of a metal*, taking into account the diversity of the known complexes, the rule is not as simple. For example the ion Ag^+ can possess the covalency $+4$, by virtue of the complex ion $Ag(CN)^{-2}$; the ion Pt^{+4} can possess the covalency $+12$, by virtue of the complex ion $PtCl_6^{-2}$.

The covalency zero exists for all free simple ions in solution. Free simple cations in solution can possess others, in addition.

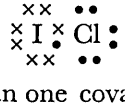
For a *simple metalloid group*, the covalency is the algebraic sum of the electrovalency and the valency: $v=z+w$. It therefore lies between 0 and 8 because z lies between $-w$ and $8-w$.

In a more general manner, the covalency lies between 0 and the maximum number of the surrounding electrons capable of assuring a state of known stability for the element concerned. This number is usually 8 for the metalloids (the octet rule). It is 2 for hydrogen. It can differ from these values in the case of metals.

The non-electrostatic bonds of a compound group are explained by the common positions of electrons with the neighbouring groups so that there are stable electronic shells for all.

If the sharing is *bilateral* then every two-electron bond (or duplet), each electron of which is supplied by a different element, is called a covalent bond. The maximum number of covalent bonds that a complex group can possess is then equal to its covalency. In other words, the covalency of a group is the maximum number of monocovalent groups with which it can be surrounded by means of covalent bonds.

For a metalloid, the number of duplets which it does not share is the complement to 4 of its covalency. In structural formulae each covalent bond is symbolized by a dash. For example, the structural formula for iodine chloride can be written



or I—Cl

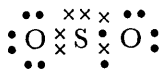
There cannot be more than one covalent bond because $v_{Cl}=v_I=1$ and there are $4-1=3$ duplets which are not shared around each of the combined atoms.

If the linkage is *unilateral* then the bond is *co-ordinate*. This is also a two-electron (or a duplet) but they are provided by the same element or *donor*, the other element being the *acceptor*.

For a metalloid group, the sum of the numbers of covalent bonds, of co-ordinate bonds and of non-shared duplets is equal to 4. It is equal to 1 for hydrogen.

In structural formulae, each co-ordinate bond is symbolized by an arrow

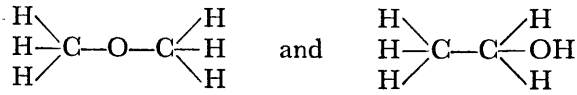
going from the donor to the acceptor. For example, the structural formula for sulphurous anhydride can be written

 or $O \leftarrow S = O$

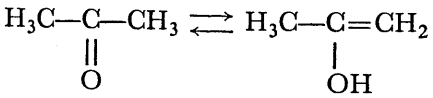
The sulphur atom can provide a second co-ordinate bond because it also possesses $4-(1+2)=1$ non-shared duplet. In general, in order to obtain the covalency in a structural formula, it is sufficient to add the number of covalent bonds to twice that of the accepted co-ordinate bonds (the co-ordinate bonds donated counting zero). For example, the structural formula for SO_3 gives the covalency 2 (1 co-ordinate bond $\times 2$) of each of the atoms of oxygen on the left, the covalency 2 (2 covalent bonds) of the sulphur atom, the covalency 2 (2 covalent bonds) of the oxygen atom on the right.

MESOMERISM. OXIDATION NUMBER

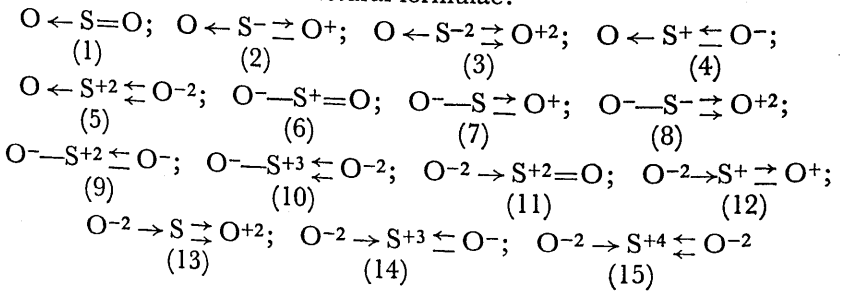
Several structural formulae can satisfy one empirical formula. *Isomerism* occurs when they differ in the spatial positions of certain atoms or ions (more explicitly of certain atomic nuclei) and when the distinct compounds may be separately isolated. For example, methyl ether and ethyl alcohol.



Tautomerism occurs when such forms co-exist in equilibrium that can reveal the anomalies of physical properties, but without being capable of isolation by virtue of the mobility of this equilibrium. For example, the ketonic and enolic forms of acetone:

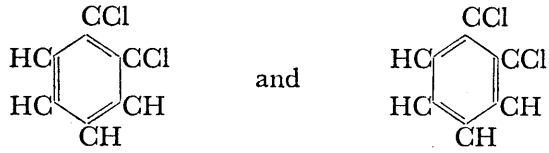


Mesomerism occurs when structural formulae satisfying the same empirical formula differ only in the localization of certain electrons. The cases of this are *a priori* numerous since, without prejudicing the stability, every covalent bond can be transformed in two different ways to a co-ordinate bond, by changing integrally the duplet corresponding either to one or other of the associated elements. The deprived group becomes acceptor and increases its electrovalency by $+1$; the enriched group becomes donor and increases its electrovalency by -1. For example, sulphurous anhydride would allow *a priori* the 15 structural formulae:

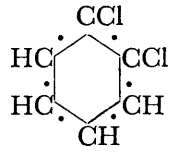


Certainly none of these forms can dissociate into simple free ions, because their co-ordinate bonds are necessary for the stability of each group.

The *principle of mesomerism* consists of admitting that such formulae imply neither the possibility of separation nor even a mobile equilibrium between the effective constituents. The real state, which cannot be described by means of the usual bonds, would be intermediate between these hypothetical limiting forms, which moreover influence the properties to a greater or lesser extent. For example, there are not two dichlorobenzenes with the formulae



The real state would be better expressed by the intermediate form



which cannot be represented by means of the usual bonds.

Except in the limiting case of purely electrostatic bonds, as in certain crystalline structures, the electrovalency of a complex ion would appear to be able to correspond to a mean over-all fractional algebraic number if applied to a large number of groups or if considered as a time mean for any one group, instead of an algebraic whole number. For example, the dipole moment of the molecule of gaseous HCl is $1{\cdot}03 \times 10^{-18}$ E.S.U. C.G.S.; electron diffraction gives the distance between the centres as $1{\cdot}26 \times 10^{-8}$ cm. From this, the numerical value of the two coupled charges can be deduced as $0{\cdot}82 \times 10^{-10}$ E.S.U. C.G.S. and after dividing by the electronic charge in E.S.U. C.G.S.,

$$z_H = -z_{Cl} = \frac{0{\cdot}82 \times 10^{-10}}{4{\cdot}81 \times 10^{-10}} = +0{\cdot}17$$

The corresponding covalencies are therefore fractional:

$$v_H = 0{\cdot}17 + 1 = 1{\cdot}17; \quad v_{Cl} = -0{\cdot}17 + 1 = 0{\cdot}83$$

The number of covalent bonds corresponds to the smallest of these magnitudes. It is thus equal to 0·83. The number of co-ordinate bonds received by the hydrogen is half the difference between its covalency and its number of covalent bonds, or $\frac{1}{2}(1{\cdot}17 - 0{\cdot}83) = 0{\cdot}17$. The number of non-shared duplets of hydrogen is $1 - 0{\cdot}83 - 0{\cdot}17 = 0$. The number of non-shared duplets of chlorine is $4 - 0{\cdot}83 - 0{\cdot}17 = 3$. It can equally be said that the bond of the usual formula H—Cl is really 83 per cent covalent and 17 per cent co-ordinate.

Such evaluations are not always possible in more complicated cases. Moreover, they are only concerned with the fundamental state of the molecules under consideration and not with their active states; these can result

from internal displacements of electrons under the action of an electric field, either applied externally (electrochemical transfers at electrodes) or emanating from a reactive molecule of another nature, and may be particularly intense during an efficient collision.

To facilitate the classification of such phenomena, it may be convenient, without forgetting the necessary exceptions, to lay down certain rules, attributing in a simple and unequivocal manner a quite fictional charge to every combined group. For this purpose, consideration is given to one of the limiting electronic forms of the compound, restoring to each of the elements except one the charge that assures its stability in the free state. The charge of the excepted element is obtained by the application of the principle of conservation of electricity. For example, without knowing the effective electrovalencies, it is considered that each oxygen has a charge of two electrons in the free ion SO_4^{-2} in solution, which will attribute to the sulphur the charge $-2-(4)(-2)=+6$ electrons.

Magnitudes of this kind constitute the *oxidation numbers* n of the groups considered; they are identical with their electrovalencies z only for free groups.

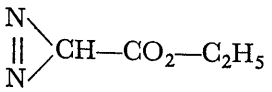
The results obtained by such a method of calculation are not however independent of the choice of the element that is taken last. For example, if first of all the oxidation number -2 is attributed to the sulphur of the ion SO_4^{-2}, the oxygen then gives an oxidation number of zero. To avoid all ambiguity, it is therefore imperative to keep to a certain order in allocating oxidation numbers to elements present in a compound. This order which partly justifies the respective positions in Mendeleeff's table is usually the following[2]:

Fundamental metals ($n=z$ for free ions). For B, $n=+3$; H ($n=+1$); F ($n=-1$); O ($n=-2$); N ($n=-3$), Cl, Br, I ($n=-1$); S, Se, Te ($n=-2$); P, As, Sb ($n=-3$).

Other elements (n obtained by difference). For example, $n_{Li}=z_{Li}=+1$ in LiH; whence $n_H=-1$. $n_F=-1$ in ClF; whence $n_{Cl}=+1$.

The order adopted here lets the case of polyatomic associations of a single element remain undetermined. For reasons of symmetry, all the electrons present would be divided equally. For example, $n_O=0$ in O_2; $n_P=0$ in P_3 (vapour); $n_{Hg}=+1$ in Hg_2^{+2} (in solution).

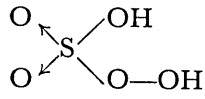
On the other hand, examination of the structural formula could, by extension of this rule, suggest exceptions to the rule whenever an element forms a bond with itself. For example, in ethyl diazoacetate,



it is convenient to give each nitrogen the oxidation number -1 rather than -3, the electrons of the double bond —N=N— being considered as equally divided.

This remark also holds for the last element considered. For example, the first carbon of ethyl diazoacetate has the oxidation number $+1$; the second, $+3$; the third, -1; the fourth, -3.

From this it appears that the oxidation number never lies outside the range of values assigned to the electrovalency. For example, in calculating the oxidation number of sulphur in Caro's acid, by using only the empirical formula SO_5H_2, it is found that $n_S = -[5(-2)+2] = +8 > z_M = +6$. On the contrary, the structural formula



shows that the two oxygens joined to one another have oxidation number -1, as in the case of oxygen in water, which brings the oxidation number of sulphur to the value $n_S = +6 = z_M$.

When the last element considered occurs several times in the compound in question, it can be given a mean oxidation number. For example, the mean oxidation number of carbon in ethyl diazoacetate is $\bar{n}_C = \frac{1}{4}(1+3-1-3) = 0$.

This can be obtained more directly as

$$\bar{n}_C = \tfrac{1}{4}\{0-[6(+1)+2(-2)+2(-1)]\} = 0$$

Such mean oxidation numbers can be fractional. For example, in the tetrathionic ion $S_4O_6^{-2}$,

$$\bar{n}_S = \tfrac{1}{4}[-2-6(-2)] = +2{\cdot}5$$

However, care should be taken not to confuse the significance of such fractional values of mean oxidation numbers with those of fractional electrovalencies of combined ions.

CONCLUDING REMARKS

The proposed definitions may be compared with those of Lange with a view to future harmonization by C.I.T.C.E. Commission C2. They differ from those of Lange in their initial assumptions, which are based on the constitution of the atom instead of on the empirical laws of classical chemistry. It may be said, in accordance with the viewpoint proposed by Piontelli, that those definitions are more of the nature of dogmatic statements than direct experimental conclusions. Nevertheless, there are many common points in the two papers, if only in the examples chosen.

The classification table of Lange does not include S, Se, Te, N, P, As, Sb. The order chosen here for the electronegativities of the metalloids is that of Pauling, with the single permutation of I (electronegativity 2·4) and S (electronegativity 2·5), which is reasonable in view of the approximation of the electronegativities.

With this exception, the order conforms entirely with that of the periodic classification.

REFERENCES

[1] KOSSEL, *Z. angew. Chem.* A59 (1947) 125.
[2] SEEL, F. *Z. Naturf.* 7b (1952) 482.

DISCUSSION

M. Haïssinsky reproche à G. Valensi d'user de distinctions entre valence, électrovalence, covalence par trop personnelles pour être communément adoptées.

G. Valensi: En matière de terminologie, les spécialistes de la chimie structurale ont malheureusement des préférences extrêmement variables d'un auteur à un autre. Il nous a paru opportun d'essayer d'y introduire un peu d'ordre. Des conventions de langage ne se discutent pas: on peut seulement juger utile ou inutile de les suivre.

M. Charlot s'inquiète du danger d'attribuer trop d'importance aux interprétations structurales, souvent ambiguës parce que basées sur des hypothèses hasardées. Il insiste sur le fait que la notion de nombre d'oxydation, qu'il préfère d'ailleurs appeler 'degré d'oxydation' doit directement s'étayer, sans parler de structure, sur une étude expérimentale minutieuse du comportement chimique, au cours de l'action des principaux réactifs.

G. Valensi (to M. Charlot): Je crains que M. Charlot ait lu un peu trop rapidement nos mémoires, car je n'arrive pas à saisir un sel de ses arguments qui soit en contradiction avec ce que je viens de dire: bien mieux, sous couleur apparente de critique, il apporte un soutien à nos idées. Je répète que le but des communications Lange et Valensi était, tout en proposant un système de *conventions* aussi claires que possible à l'électrochimiste, de montrer leurs relations avec les modes d'expression des spécialistes des structures moléculaires. Nous n'avons jamais préconisé l'usage de telles structures, pour faciliter le calcul du nombre d'oxydation: j'ai montré au contraire l'énorme difficulté d'en faire usage, puisque 15 formules différentes pourraient aussi bien exprimer la structure de l'anhydride sulfureux et que la vérité mésomérique, fort ardue à intérprêter, n'est évidemment pas pour nous d'un très grand secours, comme l'a fort bien dit M. Charlot. Le calcul du nombre d'oxydation, tel que nous le concevons, revient en définitive à la simple formule brute, question d'analyse chimique. Les cas, plus compliqués, où un élément pourrait être soudé à lui-même nécessite bien entendu une étude de comportements réactionnels, comme M. Charlot le préconise, afin qu'il en soit décidé. Il n'en demeure pas moins opportun de distinguer soigneusement le peu que nous prétendons dire sous la rubrique 'nombre d'oxydation' de tout ce que voudrait dire, sur la base des formes extrêmes qu'il envisage, le spécialiste des structures.