VALENCE RELATIONS AMONG THE METAL CARBONYLS[1,2]

ARTHUR A. BLANCHARD

Research Laboratory of Inorganic Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

Received December 9, 1939

Nickel carbonyl has frequently been described as a pure coördination compound, or as a compound in which the nickel has a valence of zero. Such a statement is very vague. Any classification of the metal carbonyls in terms of valence must rest on a very precise definition of how the valence is computed, and if it so happens that the basis for the particular method of computing the valence is questionable, then the classification according to valence is also of doubtful value.

On the other hand, the use of the effective atomic number (E.A.N.) in classifying the volatile carbonyls, nitrosyl carbonyls, and carbonyl hydrides is extremely helpful. This concept is easily and clearly defined, and the properties of the carbonyls show a marked uniformity according to this classification.

The effective atomic number is the total number of electrons held within the sphere of the atom, and includes those that the atom itself furnishes, those that are added through electron transfer, and those that are added through the establishment of covalent and coördinate bonds. Whenever the effective atomic number of the central metal atom of the compound is equal to that of an inert gas, then it is possible for the compound to be volatile. By volatile we may somewhat arbitrarily say that we mean sufficiently volatile at temperatures below 100°C. to permit molecular weight determinations by the vapor density method.

Volatility connotes lack of cohesion between molecules, that is, lack of external field. The field of the molecules of the volatile carbonyls is very much self-contained just as that of the inert gases which have the same effective atomic number as the central atoms. It is, of course, obvious that the carbonyl molecule as a whole can lack external field only when

---

[1] Presented at the Symposium on Elements in Unusual States of Valence, held at the Ninety-eighth Meeting of the American Chemical Society, Boston, Massachusetts, September, 1939.

[2] Contribution No. 79 from the Research Laboratory of Inorganic Chemistry of the Massachusetts Institute of Technology.

the net electric charge is zero and when the field of the groups surrounding the central atom is also closed inside the molecule. Thus, all of the atoms of the molecule as well as the central metal atom must have the effective atomic number of an inert gas, and there must be a high degree of symmetry in the structure of the molecule.

KINDS OF VALENCE

Valence is one of the most fruitful concepts of the chemist. It is also the one which has caused the most uncertainty and controversy.

Its first service was in clarifying the distinction between atomic and equivalent weights. At that time no cognizance was taken of the polarity of valence, and no postulate was employed beyond that of the atomic theory. In fact, valence was hardly more than a number which described the experimental fact. Would that valence could continue to serve in this simple fashion!

The knowledge of the hydrocarbons, however, rendered the whole-number concept of valence untenable without the employment of new postulates of molecular structure.

The development of electrochemistry necessitated the assignment of polarity to valence, and thereupon arose the contradictions between polar and non-polar valence which seemed impossible of reconciliation until after the postulates of the electronic constitution of atoms had been introduced. G. N. Lewis offered the brilliant suggestion that pairs of electrons could at the same time fill positions in the electron shells of two atoms and thus raise the effective atomic number of each atom to that of an inert gas.

In forming compounds or ions of elements of the first two periods or of elements not more than two or three removed from an inert gas in the long periods of the periodic series, it is invariably the rule that each atom acquires the E.A.N. of an inert gas through either sharing or transfer of electrons. In the case of transfer, the valence is without question polar.

But the metals and metalloids in the middle of the long periods are too far removed from the inert gases to acquire easily the E.A.N. of the latter. Such elements are prone to acquire what is usually regarded as a polar valence of $+2$ or $+3$ through the loss of two or three electrons. This condition is stabilized through the acquisition of an outer shell of electrons around the thus incomplete kernel of the atom. This shell consists of lone pairs of electrons donated by coördinating molecules. Shells of eight and twelve held thus between the positive kernel of the central atom and the positive cores of the coördinating molecules are possessed of a remarkable stability. These shells correspond to coördination numbers of four and six, respectively; other coördination numbers are also recognized.

$$\mathrm{Ni} \rightarrow \mathrm{Ni}^{++} + 2\mathrm{e}$$

$$\mathrm{Ni}^{++} + 4\mathrm{NH}_3 \rightarrow \mathrm{Ni \cdot 4NH_3}^{++}$$

$$\mathrm{Ni}^{++} + 4\mathrm{CN}^- \rightarrow \mathrm{Ni(CN)}_4^{--}$$

In these complexes the E.A.N. of nickel is 34.

$$\mathrm{Co} \rightarrow \mathrm{Co}^{+++} + 3\mathrm{e}$$

$$\mathrm{Co}^{+++} + 6\mathrm{NH}_3 \rightarrow \mathrm{Co \cdot 6NH_3}^{+++}$$

$$\mathrm{Co}^{+++} + 6\mathrm{CN}^- \rightarrow \mathrm{Co(CN)}_6^{---}$$

In these complexes the E.A.N. of cobalt is 36, the same as the atomic number of krypton.

The stability of the coördinating sphere of electrons is the determining factor in the formation of the complex ions, and thus in many cases the E.A.N. may be different from that of an inert gas, and the inner electron layers of the central atom may be incomplete. However, in a surprisingly large number of cases the E.A.N. of the central atom is actually the same as that of an inert gas, and it is a fair assumption that the attainment of this E.A.N. is a factor which increases the stability.

Carbon monoxide, nitric oxide, and the cyanide ion have very similar complex-forming functions (63). Uncombined their electronic structures may be represented as

:C:::O: [:C:::N:]$^-$ and   :N:⁝:O:

The extra electron which nitric oxide possesses over carbon monoxide is so completely imprisoned in the structure that the physical properties of the two substances—as well as of nitrogen :N:::N:—are very similar.[3] Nevertheless, this extra electron does have some tendency to escape, leaving the positive radical [:N:::O:]$^+$. The existence of solid crystalline nitrosyl perchlorate, $\mathrm{NOClO_4}$ (12), nitrosyl fluoborate, $\mathrm{NOBF_4}$ (64), and nitrosylsulfuric acid, $\mathrm{NO(OSO_2OH)}$, and particularly the fact that $\mathrm{NOClO_4}$ dissolved in methyl nitrate has the characteristic conductivity of a salt (8) all support this view of the positive character of the coördinating nitrosyl radical.

In linking up in complexes there are two possibilities of electron arrangement:

(I) M:C:::O: M:N:::O:

(II) M::C::O::   M::N::O::

---

[3] The complete absence of tendency of the nitrogen molecule to take part in complex building must be ascribed to the complete symmetry of the positive charges.

In case I the carbon monoxide has established one coördinate bond with the metal atom and has thus added two electrons to increase the E.A.N. The nitric oxide has established one coördinate bond with the metal atom, and the imprisoned electron has been completely transferred to the metal atom; thus three electrons have been added to increase the E.A.N.

In case II, two covalent bonds have been established between the carbon monoxide and the metal atom, but the metal atom has furnished two of the electrons so that the increase in the E.A.N. is the same as in case I,—namely, two. The nitric oxide also has increased the E.A.N. of the metal atom by three, the same as in case I.

It is interesting to note that electron diffraction studies (3, 4) of nickel carbonyl, cobalt nitrosyl carbonyl, $Co(NO)(CO)_3$, and iron nitrosyl carbonyl, $Fe(NO)_2(CO)_2$, have indicated tetrahedral structure, a straight-line arrangement of M—C—O and M—N—O, and bond distances which are in agreement with the supposition of a condition of resonance between arrangements I and II.

Likewise, the carbonyl hydrides $Co(CO)_4H$ and $Fe(CO)_4H_2$ have been subjected to electron diffraction studies by Ewens and Lister (7), with the conclusion that the same condition of resonance exists between arrangements I and II and that the hydrogen atom is situated at the end of the chain M—C—O—H

$$\begin{array}{cc} \text{M:C:::O:H} & \text{M::C::}\ddot{\text{O}}\text{:H} \\ \text{I} & \text{II} \end{array}$$

Other electron diffraction studies indicate that the structure in iron pentacarbonyl is that of a trigonal bipyramid, and that in the hexacarbonyls the structure is octahedral (5).

In table 1 are listed the known monomeric carbonyls with their effective atomic numbers figured on the supposition that each carbon monoxide adds two, each nitric oxide adds three, and each hydrogen adds one (2). All of the carbonyls in this list are volatile according to the definition we have adopted.

The polymeric carbonyls, $Fe_2(CO)_9$, $[Fe(CO)_4]_3$, $[Co(CO)_4]_2$, $[Co(CO)_3]_4$, $Ru_2(CO)_9$, and $[Ru(CO)_4]_n$ are not volatile according to our definition, although $Fe_2(CO)_9$, $[Co(CO)_4]_2$, and $Ru_2(CO)_9$ can be sublimed.

In all of these cases, however, it is possible to assign to the metal atoms the E.A.N. of an inert gas if one is allowed to save the necessary number of electrons by the linking of carbonyl groups together, thus, MCO:OCM, or to bridge two metal atoms with a single carbonyl group M:CO:M and to choose either arrangement I or arrangement II when only one of them will fit.

It is to be noted that the volatile nickel carbonyl already satisfies the tendency for the central atom to acquire the E.A.N. of 36, and that this is the only carbonyl of nickel. On the other hand, cobalt and iron form polymeric carbonyls, nitrosyl carbonyls, and carbonyl hydrides in order to satisfy this tendency.

POLAR VALENCE

Polar valence is a convenient term to use, and there can be no misunderstanding of its significance when it is applied to the charge of a monatomic ion such as Na^+ or Cl^-. When, however, it is applied to the single atoms in complexes,—either neutral molecules or ions,—we frequently run into a good deal of uncertainty. The polar valence, or electrovalence, or oxidation and reduction number, is supposedly the number of faradays necessary to convert one atomic weight of the element at the electrode to the condition in question. Other constituents which enter the complex ion are supposedly unchanged electrochemically. Too much supposition is involved to make it possible to regard polar valence as an unqualified statement of experimental fact.

TABLE 1

Effective atomic numbers in the monomeric carbonyls[4]

CARBONYL	E.A.N.	INERT GAS
BH_3CO	$5 + 3 + 2 = 10$	Ne
$Cr(CO)_6$	$24 + 12 = 36$	Kr
$Fe(CO)_5$	$26 + 10 = 36$	Kr
$Fe(CO)_2(NO)_2$	$26 + 4 + 6 = 36$	Kr
$Fe(CO)_4H_2$	$26 + 8 + 2 = 36$	Kr
$Co(CO)_3NO$	$27 + 6 + 3 = 36$	Kr
$Co(CO)_4H$	$27 + 8 + 1 = 36$	Kr
$Ni(CO)_4$	$28 + 8 = 36$	Kr
$Mo(CO)_6$	$42 + 12 = 54$	Xe
$Ru(CO)_5$	$44 + 10 = 54$	Xe
$W(CO)_6$	$74 + 12 = 86$	Rn

Chlorine and carbon monoxide both combine spontaneously with nickel to produce a new substance. Certainly we must go beyond these experimental facts to find a reason to give nickel a valence of +2 in the chloride

---

[4] Since this paper was submitted, Hieber and Schulten (Z. anorg. allgem. Chem. **243**, 164 (December, 1939)) have announced the preparation of carbonyl halides of rhenium, $Re(CO)_5X$, where X = Cl, Br, or I. These compounds have a very low vapor pressure but can be readily sublimed in a current of carbon monoxide, the iodine compound at 90°C. and the chlorine compound at 140°C. In these compounds the rhenium has the E.A.N. of 86 (radon).

and 0 in the carbonyl. Chlorine will displace iodine from iodides because chlorine is said to be more electronegative than iodine, that is, the free chlorine takes the negative electric charge away from the iodine of the iodide.

But carbon monoxide is capable of displacing halogens from a number of halides; for example, when it is passed over ruthenium triodide at 250°C., free iodine is liberated.

$$RuI_3 + 2CO \rightarrow Ru(CO)_2I_2 + \tfrac{1}{2}I_2$$

Carbon monoxide is capable even of displacing bromine and chlorine in similar reactions. All of this shows that polar valence cannot always be stated in terms of experimental fact alone.

POLAR VALENCE IN THE VOLATILE CARBONYLS

Nickel carbonyl

Neutral carbon monoxide plus neutral nickel yields neutral nickel carbonyl. This has been described as a pure coördination compound. If the carbon monoxide molecule still holds all of its original electrons, it seems justifiable to call the nickel zero-valent according to the same reasoning that, e.g., copper is divalent in the $[Cu \cdot 4NH_3]^{++}$ complex.

Cobalt nitrosyl carbonyl

Cobalt nitrosyl carbonyl has an electronic structure identical with that of nickel carbonyl, but an electron transfer has occurred; the imprisoned electron of the nitric oxide has been completely transferred to the cobalt atom to complete the pattern of its kernel electrons. In counting the polar valence of cobalt it would seem as if this transferred electron should be counted, whereas the eight electrons of the coördinate bonds should be ignored. Thus the polar valence of cobalt would be -1.

Cobalt carbonyl hydride, $(CO)_3CoCO{:}H$

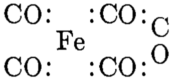
The electron of the neutral hydrogen atom has passed along the chain to take its place in the cobalt atom and again the polar valence of cobalt would be -1.

Dimeric cobalt tetracarbonyl

If neutral carbon monoxide is coördinatively added to cobalt, it might seem that the valence should be zero. However, there is undoubtedly the same shift of an electron into the kernel structure of the cobalt atom, the electrons being derived from the release of one pair when a bond such as $(CO)_3CoCO{:}COCo(CO)_3$ is established. This seems to be an argument that the valence is -1 even here.

Iron pentacarbonyl

If all five carbonyl groups are separately attached direct to the central iron atom, the latter should be assigned a valence of zero in accordance with the argument used with nickel carbonyl. If, however, the structure of iron pentacarbonyl is like that of nickel carbonyl with four carbonyl groups attached to the iron atom, and the fifth carbonyl group completing a ring



$$\begin{matrix}\text{CO:} & & \text{:CO:} & \text{C} \\ & \text{Fe} & & \\ \text{CO:} & & \text{:CO:} & \text{O}\end{matrix}$$

then the electrons released in creating the carbonyl–carbonyl bonds would be transferred completely to the iron instead of coördinatively donated, and the valence of the iron would be -2. Structure II alone, however, would fit this interpretation.

Iron nitrosyl carbonyl and iron carbonyl hydride

In $Fe(NO)_2(CO)_2$ and in $Fe(CO)_4H_2$ the valence of iron would be -2.

Trimeric iron tetracarbonyl

The same argument as with cobalt tetracarbonyl leaves the uncertainty whether to assign the valence 0 or -2 to the metal atom.

Hexacarbonyls of chromium, molybdenum, and tungsten

Here the probable octahedral arrangement with coördination number of six would indicate a valence of zero for the metal, whereas with two rings of three carbonyl groups each, i.e., with coördination number of four, the valence of -4 would be indicated.

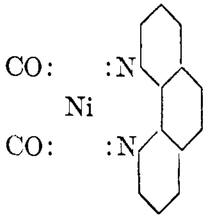
The foregoing arguments are confusing. The volatile carbonyls are so very non-polar in their character that a polar valence of the metal atom has little significance in any case. It seems to be the part of wisdom to avoid the use of polar valence with these compounds and to base our systematization of them on the concept of E.A.N. Only in the case of the hydrides, which behave as weak acids, we have the ions $Co(CO)_4^-$ and $Fe(CO)_4^{--}$, and to the ions as a whole of course a polar valence applies.

AMINE-SUBSTITUTED CARBONYLS

In the bewildering array of amine-substituted carbonyls (2), it is true in a great many of the cases that the amine molecules merely occupy the same number of coördinate positions as the displaced carbonyl groups, and thus the E.A.N. of the central atom is unchanged. For example,

$$Ni(CO)_4 + o\text{-phthr} \rightarrow Ni(CO)_2 \cdot o\text{-phthr} + 2CO$$

Here we have a chelate complex and the ortho-phenanthroline occupies two of the coördinate positions around the nickel atom.



It is noteworthy that no instance has been observed in which the carbonyl groups have been completely displaced by other neutral groups to form a pure coördination compound of the metal.

There is no record that any of the amine-substituted carbonyls displays any volatility, and no great surprise need be felt if the metal atom does not seem to possess the E.A.N. of an inert gas in a compound such as, for example, $Ni_2(CO)_3py_2$ (py = pyridine).

COMPLEX IONS CONTAINING CARBONYL AND NITROSYL GROUPS

The major influence upon the stability of a complex ion is undoubtedly the formation of a coördinating layer of electrons between the central atom and the surrounding addenda. The strength of this coördinating layer is enough to allow a considerable variation in the polar valence of the central atom; indeed some very unusual valences of the central atom have been noted in complex ions. Carbonyl and nitrosyl groups occur as addenda in a good many complex ions, and the method of coördination by means of a lone pair of electrons is entirely of the same nature as with other complex-forming groups, such as cyanide ion, chloride ion, and ammonia.

$$:C:::N: \qquad :Cl \qquad :NH_3$$

The volatile carbonyls are, in terms of the Werner coördination theory, just a special case in which the complex has a net charge of zero. Since an effective atomic number equal to that of an inert gas is an essential condition for the formation of a volatile carbonyl, it is of interest to study the relation of the E.A.N. to the stability of complex ions. The compilation in table 2 contains at least fairly well authenticated complex ions that contain carbonyl and nitrosyl groups, and for the sake of showing the trends, some other ions are included. In general, when the existence of a salt-like substance is reported which has, e.g., the composition $M_5Mn(CN)_6$, it is assumed that the complex $[Mn(CN)_6]^{-----}$ is indicated. (M represents a univalent alkali metal.)

The polar valence is figured as the difference between the atomic number and the number of electrons inside (but not including) the coördinating shell. Carbon monoxide, :C:::O:, cyanide ion, :C:::N:, chloride ion

TABLE 2

Effective atomic numbers of the central atoms in complex ions

COMPLEX ION	POLAR VALENCE	E.A.N.	REFERENCE
$M_3[Cr(CN)_6]$	+3	$24 - 3 + 12 = 33$	Pascal (47)
$M_4[Cr(CN)_6]$	+2	$24 - 2 + 12 = 34$	Pascal (48)
$M_3[Mn(CN)_6]$	+3	$25 - 3 + 12 = 34$	Pascal (39)
$M_4[Mn(CN)_6]$	+2	$25 - 2 + 12 = 35$	Pascal (39)
$M_5[Mn(CN)_6]$	+1	$25 - 1 + 12 = 36$	Manchot and Gall (27)
$M_3[Mn(CN)_5NO]$	+1	$25 - 1 + 12 = 36$	Manchot and Schmid (35)
$M_3[Fe(CN)_6]$	+3	$26 - 3 + 12 = 35$	Pascal (42)
$M_4[Fe(CN)_6]$	+2	$26 - 2 + 12 = 36$	Pascal (41, 13)
$M_3[Fe(CN)_5CO]$	+2	$26 - 2 + 12 = 36$	Manchot and Woringer (38)
$M_2[Fe(CN)_5NO]$	+2	$26 - 2 + 12 = 36$	Manchot and Woringer (38)
$M_3[Fe(CN)_5NO]$	+1	$26 - 1 + 12 = 37$	Manchot and Woringer (38)
$M_3[Fe(CN)_5NH_3]$	+2	$26 - 2 + 12 = 36$	Hoffman (11)
$M_2[Fe(CO)_4]$	−2	$26 + 2 + 8 = 36$	Blanchard (2)
$M_3[Co(CN)_6]$	+3	$27 - 3 + 12 = 36$	Pascal (46)
$[Co(NH_3)_6]Cl_3$	+3	$27 - 3 + 12 = 36$	Pascal (45)
$M_4[Co(CN)_6]$	+2	$27 - 2 + 12 = 37$	Pascal (44)
$M[Co(CO)_4]$	−1	$27 - 1 + 8 = 36$	Blanchard (2)
$M_3[Co(CN)_5CO]$	+2	$27 - 2 + 12 = 37$	Manchot and Gall (26)
$M_2[Ni(CN)_4]$	+2	$28 - 2 + 8 = 34$	Pascal (43)
$M_2[Ni(CN)_3]$	+1	$28 - 1 + 6 = 33$	Burgess (6, 1)
$M_4[Ni(CN)_4]$	0	$28 + 8 = 36$	Burgess (6)
$M_2[Ni(CN)_3NO]$	0	$28 + 8 = 36$	Manchot (18)
$M_4[Mo(CN)_8]$	+4	$42 - 4 + 16 = 54$	Pascal (49)
$M_4[Ru(CN)_6]$	+2	$44 - 2 + 12 = 54$	Howe (13)
$M_2[Ru(CN)_5NO]$	+2	$44 - 2 + 12 = 54$	Manchot and Dusing (19)
$M_2[RuCl_5NO]$	+2	$44 - 2 + 12 = 54$	Manchot and Schmid (36)
$M_3[Rh(CN)_6]$	+3	$45 - 3 + 12 = 54$	Pascal (56)
$M_2[PdCl_6]$	+4	$46 - 4 + 12 = 54$	Pascal (60)
$M_2[Pd(CN)_4]$	+2	$46 - 2 + 8 = 52$	Pascal (61)
$M_4[W(CN)_8]$	+4	$74 - 4 + 16 = 86$	Pascal (50)
$M_2[OsCl_6]$	+4	$76 - 4 + 12 = 84$	Pascal (51)
$M_3[OsCl_6]$	+3	$76 - 3 + 12 = 85$	Pascal (53)
$M_2[OsCl_5NO]$	+2	$76 - 2 + 12 = 86$	Pascal (52)
$M_4[Os(CN)_6]$	+2	$76 - 2 + 12 = 86$	Pascal (54)
$M_3[Ir(CN)_6]$	+3	$77 - 3 + 12 = 86$	Pascal (55)
$M_2[PtCl_6]$	+4	$78 - 4 + 12 = 86$	Pascal (57)
$M_2[PtCl_2(CN)_4]$	+4	$78 - 4 + 12 = 86$	Pascal (59)
$M_2[Pt(CN)_4]$	+2	$78 - 2 + 8 = 84$	Pascal (58)

:Cl, and ammonia, :NH_3, each donates two electrons to the coördinate shell and does not affect the polar valence. Nitric oxide is assumed to lose one electron entirely to the metal and thus lower the polar valence of the latter, the remaining positive nitrosyl group :N:::O: contributing two electrons to the coördinate shell.

It is noticed at once that in a great many of these complex ions the E.A.N. is actually that of an inert gas. In cases in which the E.A.N. is different there is almost invariably a manifest trend towards the stable number.

For example, in the complex iron cyanides the ferricyanide ion, $Fe(CN)_6^{---}$ (E.A.N. = 35), tends to gain an electron to change to the ferrocyanide ion (E.A.N. = 36). The replacement of one cyanide ion by a carbonyl group in the ferricyanide ion, thus forming the ion $Fe(CN)_5CO^{---}$, again raises the E.A.N. to 36. Introduction of ammonia to replace a cyanide ion likewise raises the E.A.N. to 36. The well-known nitroprusside ion, $Fe(CN)_5NO^{--}$, bears two negative charges, thus giving to the central atom the E.A.N. of 36. The triply charged ion, $Fe(CN)_5NO^{---}$, in which the E.A.N. is 37, can be prepared, but it is unstable and goes over spontaneously to the common nitroprusside (38).

Among the cobalt cyanides the cobaltocyanide ion, $Co(CN)_6^{----}$ (E.A.N. = 37), tends strongly to go over into the cobaltic cyanide ion, $Co(CN)_6^{---}$, with an E.A.N. of 36.

In preparing the carbonyl-substituted complex $Co(CN)_5CO^{---}$ (E.A.N. = 37) Manchot and Gall took extreme precautions to suppress the spontaneous evolution of hydrogen, which would have increased the valence of cobalt from 2 to 3. In all probability the ion $Co(CN)_5CO^{--}$ (E.A.N. = 36) would be formed if it were given a fair chance.

Among the nickel cyanides, the E.A.N. of nickel in the rather unstable $Ni(CN)_4^{--}$ is 34, but the tendency towards an E.A.N. of 36 is shown in the very unusual ion $Ni(CN)_4^{----}$, in which the polar valence of nickel is zero (6).

W. M. Burgess has found that when a solution of potassium nickelocyanide in liquid ammonia is treated with excess of potassium, a yellow precipitate of the composition $K_4Ni(CN)_4$ is formed; with the $K_2Ni(CN)_4$ in excess, however, a red precipitate of $K_2Ni(CN)_3$, previously described by Bellucci (1), is obtained. Burgess also has found that ferricyanides (E.A.N. = 35) are reduced to ferrocyanides (E.A.N. = 36), but that ferrocyanides are not reduced further by liquid ammonia solutions of sodium, potassium, or calcium.

Among the cyanides of manganese the trend is shown in the formation of $Mn(CN)_6^{-----}$ (E.A.N. = 36), a most unusual ion with five negative charges, and in the ion $Mn(CN)_5NO^{---}$, in which manganese also has the unusual polar valence of +1.

Among the cyanides of chromium only the chromo- and the chromicyanide ions have been reported, but the trend would seem to point to the hexavalent ion $[Cr(CN)_6]^{------}$, in which chromium would be zerovalent.

Molybdenum and tungsten show, respectively, the E.A.N. = 54 of xenon and the E.A.N. = 86 of radon in the complexes $[Mn(CN)_8]^{----}$ and $[W(CN)_8]^{----}$, which have the unusual coördination number of eight.

Among the platinum metals the prevalence of the E.A.N. of xenon and radon is very obvious. With divalent palladium and platinum, as also with nickel, such an E.A.N. is structurally impossible, and we should look to see if compounds corresponding to $K_4[Ni(CN)_4]$ and $K_2[Ni(CN)_3NO]$ can be prepared.

TABLE 3

Carbonyl halides of heavy metals

COMPOUND	POLAR VALENCE	E.A.N.	REFERENCE
$CuCO \cdot X$	+1	29 − 1 + 4 = 32	(23)
$CuNO \cdot X_2$	+1	29 − 1 + 6 = 34	(14)
$Ru(CO)_2 \cdot X_2$	+2	44 − 2 + 8 = 50	(28)
$RuCO \cdot Br$	+1	44 − 1 + 4 = 47	(21)
$PdCl_2 \cdot CO$	+2	46 − 2 + 6 = 50	(31)
$PdCl_2 \cdot 2NO$	0	46 + 8 = 54	(37)
$OsX_2 \cdot 3CO$	+2	76 − 2 + 10 = 84	(29)
$IrCl_2 \cdot 2CO$	+2	77 − 2 + 8 = 83	(24)
$PtCl_2 \cdot CO$	+2	78 − 2 + 6 = 82	(17, 62)
$PtCl_2 \cdot 2CO$	+2	78 − 2 + 8 = 84	(17, 62)
$AuCl \cdot CO$	+1	79 − 1 + 4 = 82	(25)
$Fe(NO)_2I$	−1	26 + 1 + 6 = 33	(9, 22)
$Co(NO)_2I$	−1	27 + 1 + 6 = 34	(10)

CARBONYL HALIDES

Carbon monoxide and nitric oxide combine with the salts, notably the halides, of the heavy metals, forming compounds which vary a good deal in character but in general are sublimable (although not volatile in terms of our arbitrary standard), lack pronounced salt-like character, are soluble in organic solvents, are hydrolyzed or decomposed by water, and possess unusual valences of the metal atom.

The valence and the E.A.N. in table 3 are figured on the basis of the monomeric formula and on the assumption that nitric oxide has transferred one electron and donated two electrons to the metal atom. The lack of volatility and for the most part the absence of molecular weight determinations of any kind deprives the E.A.N. numbers of significance, because it is impossible to estimate how many electrons are gained by CO or NO bridges between metal atoms. Further compounds, in which no attempt is made to assign a valence or an E.A.N., add still more to the confusion of the picture: $Ag_2SO_4 \cdot CO$ (16, 32), $RhCl_2 \cdot RhO \cdot 3CO$ (30), $RhCl_2 \cdot RhO \cdot 3NO$ (34), $2PtCl_2 \cdot 3CO$ (17, 62), $FeSO_4 \cdot NO$ (40), $Fe(NO)_4$ (20), $Ru(NO)_{4-5}$ (33), and $COHg(OC_2H_5)(COOCH_3)$ (15).

The only sure generalization which can be made is that carbonyl and nitrosyl groups have a strong tendency to coördinate with heavy-metal atoms and that in general such coördination enhances the stability of an unusual valence state of the metal.

It probably is unwarranted to assume that always one electron is completely transferred to the metal when nitric oxide coördinates, and hence the polar valences derived on that basis should be taken with some reservation.

It is interesting to note that in the similar pair of nitrosyl compounds $Fe(NO)_2I$ and $Co(NO)_2I$ the atomic number of the metal has no effect in determining the structure of the complex, whereas in the pair $K_3[Mn(CN)_5NO]$ and $K_2[Fe(CN)_5NO]$ the tendency to acquire the E.A.N. of krypton is sufficient to determine the polar valence of the metal and the charge of the complex ion.

In the pair of compounds $RhCl_2 \cdot RhO \cdot 3CO$ and $RhCl_2 \cdot RhO \cdot 3NO$ the carbonyl and nitrosyl groups are interchangeable (34), and either nitric oxide or carbon monoxide is able to replace the other without breaking the structure of the compound.

SUMMARY

The use of the term "valence" involves many uncertainties unless the method of computing the valence is very carefully detailed in every case.

This is particularly true when we are dealing with the volatile carbonyls. Indeed any method of computing the valence with these compounds is so involved in uncertain hypotheses that it would seem better to avoid altogether the use of the term.

The concept of effective atomic number (E.A.N.), however, proves an excellent basis for classifying the volatile carbonyls.

In the formation of complex ions containing carbonyl and nitrosyl groups, two factors are apparent: first, the tendency to form a stable coördinating layer of electrons between the central atom and the surrounding addenda; second, the tendency of the central atom to acquire the E.A.N. of an inert gas. It is unmistakable that the ions in which this second tendency has also functioned are more stable than those in which the first tendency alone has been satisfied.

The non-volatile or little-volatile carbonyl and nitrosyl halides and salts

of the heavy metals present a very incomprehensible picture. Too little is known of their properties to draw any valid conclusions. In general, the coördination of carbonyl and nitrosyl groups appears to stabilize the otherwise less stable polar valence of the heavy metal. But even this generalization is subject to the uncertainty of the definition of the polar valence.

REFERENCES[5]

(1) Bellucci, I. and Corelli, R.: Z. anorg. Chem. **86**, 88 (1914).
(2) Blanchard, A. A.: Chem. Rev. **21**, 3 (1937).
(3) Brockway, L. O., and Anderson, J. S.: Trans. Faraday Soc. **33**, 1233 (1937).
(4) Brockway, L. O., and Cross, P. C.: J. Chem. Phys. **3**, 828 (1935).
(5) Brockway, L. O., Ewens, R. V. G., and Lister, M. W.: Trans. Faraday Soc. **34**, 1350 (1938).
(6) Burgess, W. M.: Paper read at the Symposium on Elements in Unusual States of Valence, held at the Ninety-eighth Meeting of the American Chemical Society, Boston, September, 1939.
(7) Ewens, R. V. G., and Lister, M. W.: Trans. Faraday Soc. **35**, 681 (1939).
(8) Hantzsch, A., and Berger, K.: Z. anorg. allgem. Chem. **190**, 321 (1930).
(9) Hieber, W., and Anderson, J. S.: Z. anorg. allgem. Chem. **211**, 132 (1933).
(10) Hieber, W., and Marin, R.: Z. anorg. allgem. Chem. **240**, 241 (1939).
(11) Hoffman, K. A.: Z. anorg. Chem. **10**, 264 (1895); Ann. **312**, 1 (1900).
(12) Hoffman, K. A., and Zedwitz, G. A.: Ber. **42**, 2031 (1909).
(13) Howe, J. L.: J. Am. Chem. Soc. **18**, 981 (1896).
(14) Manchot, W.: Ber. **47**, 1601 (1914).
(15) Manchot, W.: Ber. **53**, 984 (1920); **54**, 571 (1921).
(16) Manchot, W.: Ber. **57**, 1157 (1924).
(17) Manchot, W.: Ber. **58**, 2518 (1925).
(18) Manchot, W.: Ber. **59**, 2448 (1926).
(19) Manchot, W., and Dusing, J.: Ber. **63**, 1226 (1930).
(20) Manchot, W., and Enk, E.: Ann. **470**, 275 (1929).
(21) Manchot, W., and Enk, E.: Ber. **63**, 1635 (1930).
(22) Manchot, W., and Fischer, H.: Dissertation, Technische Hochschule, München, 1937; Z. anorg. allgem. Chem. **240**, 242 (1939).
(23) Manchot, W., and Friend, J. N.: Ann. **359**, 100 (1908).
(24) Manchot, W., and Gall, H.: Ber. **58**, 232 (1925).
(25) Manchot, W., and Gall, H.: Ber. **58**, 2175 (1925).
(26) Manchot, W., and Gall, H.: Ber. **59**, 1056 (1926).
(27) Manchot, W., and Gall, H.: Ber. **61**, 1135 (1928).
(28) Manchot, W., and König, J.: Ber. **57**, 2130 (1924).
(29) Manchot, W., and König, J.: Ber. **58**, 229 (1925).
(30) Manchot, W., and König, J.: Ber. **58**, 2173 (1925).
(31) Manchot, W., and König, J.: Ber. **59**, 883 (1926).
(32) Manchot, W., and König, J.: Ber. **60**, 2183 (1927).
(33) Manchot, W., and Manchot, W. J.: Z. anorg. allgem. Chem. **226**, 385 (1936).

---

[5] A recent review of the volatile metal carbonyls (2) contains a fairly extensive bibliography. In the present paper references contained in the earlier review are not always repeated.

(34) MANCHOT, W., AND PFLAUM, W.: Ber. **60**, 2180 (1927).
(35) MANCHOT, W., AND SCHMID, H.: Ber. **59**, 2360 (1926).
(36) MANCHOT, W., AND SCHMID, H.: Z. angew. allgem. Chem. **216**, 99 (1933).
(37) MANCHOT, W., AND WALDMÜLLER, A.: Ber. **59**, 2363 (1926).
(38) MANCHOT, W., AND WORINGER, P.: Ber. **45**, 2869 (1912); **46**, 3514 (1913).
(39) PASCAL, PAUL: *Traitè de Chimie Minerale*, Vol. IX, p. 544. Masson et Cie., Paris (1933).
(40) Reference 39, p. 840.
(41) Reference 39, pp. 858, 886.
(42) Reference 39, pp. 859, 887.
(43) PASCAL, PAUL: *Traitè de Chimie Minerale*, Vol. X, p. 207. Masson et Cie., Paris (1933).
(44) Reference 43, p. 409.
(45) Reference 43, p. 722.
(46) Reference 43, p. 961.
(47) Reference 43, p. 1071.
(48) Reference 43, p. 1089.
(49) PASCAL, PAUL: *Traitè de Chimie Minerale*, Vol. XI, p. 39. Masson et Cie., Paris (1932).
(50) Reference 49, p. 113.
(51) Reference 49, p. 365.
(52) Reference 49, p. 370.
(53) Reference 49, p. 376.
(54) Reference 49, p. 380.
(55) Reference 49, p. 505.
(56) Reference 49, p. 585.
(57) Reference 49, p. 669.
(58) Reference 49, p. 674.
(59) Reference 49, p. 675.
(60) Reference 49, p. 805.
(61) Reference 49, p. 809.
(62) SCHÜTZENBERGER: Compt. rend. **70**, 1134, 1287 (1870).
(63) SIDGWICK, N. V., AND BAILEY, R. W.: Proc. Roy. Soc. (London) **144**, 521 (1934).
(64) WILKE-DÖRFURT, E., AND BALZ, G.: Z. anorg. allgem. Chem. **159**, 219 (1927).