SCIENCE

Vol. 94 Friday, October 3, 1941 No. 2440

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS

Lancaster, Pa. Garrison, N. Y.
New York City: Grand Central Terminal

Annual Subscription, $6.00 Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the Association may be secured from the office of the permanent secretary in the Smithsonian Institution Building, Washington, D. C.

THE METAL CARBONYLS[1,2]

By Professor ARTHUR A. BLANCHARD

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

This meeting is to do honor to a man who was a great scientist, who was later, also, a great administrator, and who, when he reached the age when he could surrender his administrative duties and could enjoy the leisure and rest which he had so fully earned, chose to devote his great energy to the cause of the orderly development of the science of chemistry he loved. Edgar Fahs Smith exemplified the most truly scientific attitude towards chemistry. He championed the importance of accurate finding and recording of facts, and he encouraged the use of theories only as they helped to clarify and classify the facts. A favorite remark of his was to the effect that theories come and theories go, but facts live on forever.

It is, I think, entirely fitting that I should do honor to Professor Smith in telling you the facts about an unusual class of substances, the metal carbonyls, in which I have taken a particular interest, and to show how certain generalizations have helped to some extent to classify and define the relationship among the carbonyls.

Nickel Carbonyl

Nickel carbonyl was discovered by Mond in 1890, and iron pentacarbonyl was discovered shortly thereafter. These strange substances were a challenge to

---

[1] Edgar Fahs Smith Memorial Lecture at the University of Pennsylvania May 23, 1941.

[2] Fairly complete literature references may be found in *Chemical Reviews,* 21: 3, 1937, and 26: 409, 1940.

the intelligence of chemists, for, except for the law of definite proportion, they violated every generalization known to chemists at that time.

Nickel carbonyl is formed by the direct combination of carbon monoxide with metallic nickel. Spongy nickel, freshly prepared by gently heating nickel formate in hydrogen, will at room temperature take on carbon monoxide greedily with the formation of nickel carbonyl, $Ni(CO)_4$. On the other hand, compact nickel which has been in contact with the air will not react perceptibly with carbon monoxide. It is this fact which explains why the carbonyls were not discovered earlier.

Nickel carbonyl is a water-white, very mobile and very volatile liquid. It has about the same volatility as ethyl ether, and since inhaling traces of its vapors causes death or incurable impairment of the nerves and the vital organs, it should never be handled except with extreme caution.

Nickel carbonyl forms at room temperature; it also dissociates at moderate temperatures. It is interesting to observe a delivery tube in the open laboratory through which carbon monoxide laden with nickel carbonyl vapor is passing. A thin layer of metallic nickel may deposit on the inside of the tube as a brilliant mirror. Perhaps soon the load of nickel carbonyl vapor may fall off and nearly pure carbon monoxide will be passing. In such a case the black mirror will appear to evaporate.

Nickel carbonyl meets the definitions of a chemical compound. Nickel and carbon monoxide unite in definite proportions and the physical properties of the compound are totally different from the properties of either nickel or carbon monoxide. Yet chemically nickel carbonyl behaves like uncombined nickel on the one hand and like uncombined carbon monoxide on the other hand.

Chlorine and bromine react instantly and quantitatively with nickel carbonyl, forming nickel halide, and all the carbon monoxide is set free. Iodine, sulfur and oxygen react similarly, although not quite so decisively. On the other hand, when nickel carbonyl is inhaled and gets into the blood stream, carbon monoxide instantly combines with the hemoglobin and free nickel is left. It is, in fact, this colloidal nickel in the blood which is so destructive. With Grignard reagents nickel carbonyl reacts instantly with a precipitation of black nickel and the formation of the compounds that would be expected from the reaction of carbon monoxide and Grignard reagent. Nickel carbonyl is insoluble in water but generally soluble in all proportions in organic solvents. It is unattacked by dilute acids and alkalies.

Volatile Carbonyls

The description of the method of formation and of the chemical and physical properties of nickel carbonyl could be applied with only minor modifications to all the metal carbonyls.

The closest analogy to the type of chemical combination existing in the carbonyls is shown by hydrates, which dissociate easily into water and anhydrous salts.

To-day we have quite an impressive list of volatile carbonyls, as shown in Table 1; the volatility is sufficient for molecular weight determinations to be made by the vapor density method at temperatures generally below 100° centigrade.

TABLE 1

Volatile Carbonyls

Compound	Vapor pressure mm	begins to decompose at °C
$Ni(CO)_4$	261 at 15° C	60
$Fe(CO)_5$	15 at 25° C	150
$Ru(CO)_5$	Very volatile	–15
$Cr(CO)_6$	1.0 at 48° C	130
$Mo(CO)_6$	2.3 at 55° C	150
$W(CO)_6$	1.2 at 67° C	150
$Co(CO)_3NO$	56 at 16° C	< 100°
$Fe(CO)_2(NO)_2$	4.5 at 0° C	< 50°
$Co(CO)_4H$	Very volatile	–33°
$Fe(CO)_4H_2$	11 at –10° C	< –33°
$Re(CO)_5Cl$	sublimes at < 100° C	> 100°

Importance of the Property of Volatility

The property of volatility was one of the first of the properties of matter to be recognized. In the interesting old prints taken from the time of the alchemists we always find the alembic (or still) prominently displayed, thus showing the importance attributed to the property of volatility by the earliest scientists.

To-day the enthusiasm for the more recently recognized properties of matter is so great that I believe that the simple but important property of volatility is too much neglected. I refer to such properties as x-ray diffraction, absorption and emission spectra (both x-ray and optical), electron diffraction, magnetic susceptibility, dielectric constant, Raman spectrum and, perhaps the newest of all, resonance, which in fact is not a property at all but rather an imaginary condition remotely related to those properties that can be measured experimentally.

Volatility signifies lack of cohesion between molecules. There is really little fundamental difference between chemical affinity and cohesion. We are accustomed rather arbitrarily to regard the phenomenon as due to chemical affinity when we find definite proportion, and simply as due to cohesion when the proportions are variable. But both chemical affinity and cohesion are due to the same cause, namely, the field of atoms and molecules and ultimately the field of the nucleus and electrons within the atom.

With the inert gases the tremendous fields of the nucleus and electrons almost completely neutralize each other or, in other words, the lines of force are completely closed within the atom, and neither cohesion nor chemical affinity are manifest to any marked extent. The atoms of all other elements possess external fields. Where definite groups of atoms can form in which the fields of the different atoms are mutually neutralized, there is little cohesion between the molecules and the compounds are volatile. Thus when we try to study the nature of valence and chemical affinity among the volatile carbonyls the problem is simplified in that all the forces are self-contained within the molecule.

Valence and Effective Atomic Number

The concept of valence was first introduced to clarify the distinction between atomic and equivalent weights, and at that time no cognizance was taken of the polarity of valence. The knowledge of the hydrocarbons 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. In 1916 G. N. Lewis offered the seemingly absurd suggestion that pairs of electrons could at the same time fill positions in the outer electron shells of two atoms. Atoms are prone to gain or lose electrons until the number in the outer shell or valence layer is eight. Langmuir in 1919 contributed largely in clarifying this "octet" theory of valence. C. R. Bury in 1921 extended this theory to the heavier elements, and showed more specifically how the inert gases served as the fixed reference points of the theory, but how the elements in the mid-parts of the long periods might possess variable atom kernels.

Later Sidgwick, in the course of the study of complex ions, introduced the term "Effective Atomic Number" (E.A.N.) to denote the total number of electrons, both shared and unshared, possessed by an atom. The electronic valence theory as developed by Lewis, Langmuir and Bury may be simply stated in terms of E.A.N. All elements tend to enter the state of combination in such a way as to make the E.A.N. coincide with that of an inert gas.

If this rule is applied to the volatile carbonyls, it is found that in each case the E.A.N. of the central atom is that of an inert gas if in counting the E.A.N. we adopt the reasonable postulates that each carbon monoxide molecule donates two electrons, each nitric oxide molecule donates two electrons and transfers one electron, each hydrogen atom donates one electron and each chlorine atom withdraws one electron to acquire its own octet and then donates or shares two of its octet.

TABLE 2

Effective Atomic Numbers

BH_3CO	5 + 3 + 2	10	Ne
$Ni(CO)_4$	28 + 8	36	Kr
$Fe(CO)_5$	26 + 10	36	Kr
$Ru(CO)_5$	44 + 10	54	Xe
$Cr(CO)_6$	24 + 12	36	Kr
$Mo(CO)_6$	42 + 12	54	Xe
$W(CO)_6$	74 + 12	86	Rn
$Co(CO)_3(NO)$	27 + 6 + 3	36	Kr
$Fe(CO)_2(NO)_2$	26 + 4 + 6	36	Kr
$Co(CO)_4H$	27 + 8 + 1	36	Kr
$Fe(CO)_4H_2$	26 + 8 + 2	36	Kr
$Re(CO)_5Cl$	75 + 10 − 1 + 2	86	Rn

It is noteworthy that nickel carbonyl, $Ni(CO)_4$, which is the most volatile of all the carbonyls, is the only carbonyl of nickel.

If monomeric tetracarbonyls or iron and cobalt were to exist, the E.A.N. would not be 36. But the modifications of tetracarbonyls, $Fe(CO)_2(NO)_2$, $Fe(CO)_4H_2$ $Co(CO)_3(NO)$ and $Co(CO)_4H$, all of which are known and are very volatile, do show an E.A.N. of 36 for the central atom. Furthermore, iron and cobalt are prone to form polymeric tetracarbonyls, $[Fe(CO)_4]_3$ and $[Co(CO)_4]_2$, which are only very slightly, if at all, volatile. To iron and cobalt in these polymers we may easily ascribe the E.A.N. of 36 by properly placing the shared electrons which bind the polymers together.

A complete list of the polymeric carbonyls is given in table 3.

TABLE 3

Polymeric Carbonyls

$Fe_2(CO)_9$
$[Fe(CO)_4]_3$
$[Co(CO)_4]_2$
$[Co(CO)_3]_4$
$Ru_2(CO)_9$
$[Ru(CO)_4]_n$

Of these, the ennea carbonyls, $Fe_2(CO)_9$ and $Ru_2(CO)_9$, and the tetracarbonyl $[Co(CO)_4]_2$ may be sublimed without decomposition, but all the molecular weights are determined only by the freezing point lowering method in organic solvents.

Metal Carbonyls as Coordination Compounds

It is interesting to note that Albert Werner's system of coordination was first proposed at about the time of the discovery of nickel and iron carbonyls. However, it was some time before it was realized that the carbonyls fitted into this system. The earlier grotesque attempt to assign a structure to the carbonyls would often postulate ring structures with the metal atom a member of the ring. However, when the coordination system began to assume the stature of a real theory, through the application to it, notably by Sidgwick, of the newly developed ideas of the electronic structure of matter, it became apparent that the carbonyls belonged properly in the coordination theory with the metal atom in the center of the coordinate group. A notable difference between the carbonyls and all other coordination complexes remained, however, in that the valence (electrovalence) of the metal atom of the carbonyls is zero, whereas always the valence of the metal atom in other complexes is a positive number.

The central position of the metal-atom in the carbonyl complex is supported by recent studies of electron diffraction, which indicate that: in the compounds with four addenda the four groups are situated at the corners of a tetrahedron surrounding the metal atom; in the penta carbonyls the structure is that of a trigonal bipyramid and in the hexacarbonyls the structure is octahedral; the atom arrangement M–C–O and M–N–O form straight lines, the hydrogen atoms lie at the end of the chain M–C–O–H; and the bond distances are such as to be in harmony with a condition of resonance between the structures

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

The extreme resemblance of carbon monoxide and nitric oxide in physical properties is taken to indicate a similarity in constitution. The most commonly accepted electronic structure of carbon monoxide is shown in the formula

$$\text{:C:::O:}$$

Nitric oxide has one more electron, which is somehow tucked away in the molecule without a profound effect on the physical properties. When coordination of carbon monoxide with a metal atom takes place, the lone pair on the carbon atom enters the coordination layer of the metal atom and thus the E.A.N. of the metal is increased by two. When nitric oxide coordinates, the lone pair of the nitrogen atom enters the coordination layer of the metal atom and the extra electron of the nitric oxide is transferred completely and thus the E.A.N. of the metal is increased by three. In the resonating structures it is to be noted that two of the electrons of the double bond between the metal and carbonyl group or the metal and the nitrosyl group came from the metal so that the E.A.N. of the metal and, in fact, of the carbon oxygen and nitrogen, remains unchanged by the resonance.

When, a moment ago, we spoke of zero valence in the carbonyls we spoke in rather vague terms although we would probably be understood in the sense that was intended. Whenever water molecules (in hydrates), cyanide ions (in complex ions), carbon monoxide molecules (in carbonyls), coordinate, the coordinating electrons are counted as still belonging exclusively to the addenda when the polar valence of the central atom is counted and thus the valence becomes the difference between the atomic number (nuclear charge) and the number of electrons inside of the coordinate layer. According to this method of counting, the valence of the metal would be zero in $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, but it would be minus one in $Co(CO)_3NO$ and $Co(CO)_4H$ and minus two in $Fe(CO)_2(NO)_2$ and $Fe(CO)_4H_2$.

No one should disagree with the appraisal of such valences as the height of absurdity. We have simply illustrated the seeming absurdities we reach when we give the result of our own counting of valence if we do not very exactly specify our method of counting.

Non-Volatile Carbonyls

In addition to the volatile carbonyls there are a great many complex compounds or salts in which carbon monoxide and nitric oxide are present and obviously bound as coordinated addenda in the same manner as in the volatile carbonyls. Table 4 contains a list of some of the more important of these where X stands for a halogen atom.

TABLE 4

Non-Volatile Carbonyl and Nitrosyl Complexes

$CuX \cdot CO$
$CuX_2 \cdot NO$
$RuX_2 \cdot 2CO$
$RuBr \cdot CO$
$PdCl_2 \cdot CO$
$OsX_2 \cdot 3CO$
$IrCl_2 \cdot 2CO$
$PtCl_2 \cdot CO$
$2PtCl_2 \cdot 3CO$
$AuCl \cdot CO$
$FeI \cdot 2NO$
$CoI \cdot 2NO$
$Ag_2SO_4 \cdot CO$
$RhCl_2 \cdot RhO \cdot 3CO$
$RhCl_2 \cdot RhO \cdot 3NO$
$FeSO_4 \cdot NO$
$CO \cdot Hg(OC_2H_5)(COOCH_3)$

Some of these compounds may be sublimed without decomposition but none have an appreciable volatility at ordinary temperatures. There is no apparent dependence of these compounds upon the effective atomic number, but since these compounds are not volatile and the molecular weight of few of them has been determined, it is impossible to draw definite conclusions whether the E.A.N. is or is not a dominating factor in their existence.

Complex Ions and Effective Atomic Number

At all events the effective atomic number is very clearly a dominant influence in the formation of the volatile carbonyls, and also from the other point of view the regularities observed among the volatile carbonyls confirms a wider potency of the influence of the E.A.N. than had been suspected from the composition of the simpler compounds of the transition elements. Elements within three places of the inert gases are conceded to acquire the electron structure of the inert gases, but the elements in the middle parts of the long periods have been generally conceded to acquire polar valence through a transfer of electrons into incomplete inner layers, leaving generally two or three electrons only in the valence layer.

Complete loss of these valence electrons has generally been regarded as the explanation of polar valence in such ions as are commonly formulated as Fe^{++}, Fe^{+++}, Mn^{++}, Cr^{+++}, Co^{++}, Ni^{++}, etc., and little evidence has been apparent that the effective atomic number exerts any influence in forming compounds of the transition elements.

But with the evidence of the volatile carbonyls and in view of the fact that carbon monoxide and nitric oxide enter the composition of many complex ions it seemed fitting to reexamine the list of complex ions to see if any influence of the E.A.N. could be traced. I believe that the evidence presented in Tables 5–9 will be quite convincing that there is such an influence.

There is a good deal of similarity between volatility and ionization. In volatile substances the field is self-contained within the molecule and the lack of external field accounts for the lack of cohesion between the molecules. With charged ions there is a great external field and there can be no chance of volatility outside the confines of the solution. But within the solution ions may exist when the electrostatic field is uniform, that is, when the charge is symmetrically distributed over the ion.

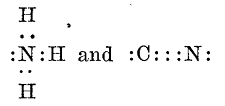
Nickel atoms are usually pictured as forming ions through the loss of electrons:

$$Ni \rightarrow Ni^{++} + 2\,\theta.$$

The fact that bare Ni^{++} ions do not exist in more than the most infinitesimal concentrations, if at all, does not seem to bother the authors of text-books. The only excuse for writing Ni^{++}—and it is seldom apparent that the authors realize any need for an excuse—is that the number n of water molecules in the hydrate $Ni \cdot nH_2O^{++}$ is unknown. It ought to be apparent from the knowledge of complex ions such as

$$Ni \cdot 4NH_3^{++}$$
$$Ni \cdot (CN)_4^{--}$$

that the ion Ni^{++} can not exist in water without surrounding itself with coordinating H_2O molecules. If the coordinating groups



$$\overset{\displaystyle H}{\underset{\displaystyle H}{:\ddot{\underset{..}{N}}:}}H \quad \text{and} \quad :C:::N:$$

are joined to the nickelous ion by means of the lone pairs it is obvious that each addendum adds 2 to the E.A.N. which thus becomes

$$28 - 2 + 8 = 34.$$

Obviously, the coordinating shell of eight electrons between the positive kernel of the Ni atom and the positive kernels of the N or C atoms imparts a certain stability to the structure. These complex nickelous ions are moderately stable but let us compare their stability with that of the cobaltic complex ions.

$$Co \rightarrow Co^{+++} + 3\,\theta$$
$$Co^{+++} + 6\,NH_3 \rightarrow Co \cdot 6\,NH_3^{+++}$$
$$CO^{+++} + CN^{-} \rightarrow Co(CN)_6^{---}$$

These cobaltic complexes are extraordinarily stable and once formed they are broken down only by very strenuous chemical treatment. In them the E.A.N. of cobalt is

$$27 - 3 + 12 = 36.$$

It might of course be accidental, and due to some other cause, that in these two cases the complex with the E.A.N. of krypton is much more stable, but let us proceed to see how generally such a relation holds.

COMPLEXES OF IRON

Of the two cyanide complexes of iron the ferricyanide (E.A.N. = 37) is the less stable and it tends to go over to the ferrocyanide (E.A.N. 36). In Table 5 are listed several of the substituted cyanide complexes of iron where M represents a univalent alkali metal.

TABLE 5

COMPLEXES OF IRON

$M_4[Fe(CN)_6]$	26 − 2 + 12	36
$M_3[Fe(CN)_6]$	26 − 3 + 12	35
$M_2[Fe(CN)_5NO]$	26 − 2 + 12	36
$M_3[Fe(CN)_5NH_3]$	26 − 2 + 12	36
$M_3[Fe(CN)_5NO]$	26 − 1 + 12	37
$M_2[Fe(CO)_4]$	26 + 2 + 8	36

Treatment of either the ferrocyanide or ferricyanide with hot concentrated nitric acid yields the fairly stable nitro prusside complex, E.A.N. 36, and sodium nitro prusside can be crystallized from the solution. If this complex is treated with ammonia, the nitric oxide is substituted by ammonia $M_2[Fe(CN)_5NO] + 3\,NH_3 + H_2O \rightarrow NH_4M_2[Fe(CN)_5NH_3] + NH_4NO_2$ and the E.A.N. in the new complex is still 36.

But if the ammonia-substituted complex is treated with NO in acidified solution the freely running reaction $HC_2H_3O_2 + M_3[Fe(CN)_5NH_3] + NO \rightarrow M_3[Fe(CN)_5NO] + NH_4C_2H_3O_2$ gives rise to a different nitro prusside complex in which the E.A.N. is 37. But this complex is very unstable and it spontaneously changes into the ordinary nitro prusside within a short time.

COMPLEXES OF COBALT

Contrasted with the cyanide complexes of iron, the cobaltocyanide complex (E.A.N. 37) is the unstable compound of cobalt and this has a very strong tendency to go over into the cobalticyanide.

TABLE 6

COMPLEXES OF COBALT

$M_3[Co(CN)_6]$	27 − 3 + 12	36
$M_4[Co(CN)_6]$	27 − 2 + 12	37
$M_3[Co(CN)_5CO]$	27 − 2 + 12	37
$[Co(NH_3)_6]X_3$	27 − 3 + 12	36
$M[Co(CO)_4]$	27 + 1 + 8	36

In the preparation of the carbonyl substituted double cyanide Manchot and Gall took extreme precaution to prevent possible oxidation to the cobaltic state and hence no chance was given to form the compound $M_2[Co(CN)_5CO]$ in which the E.A.N. would be 36. In our own laboratories all attempts to prepare either this complex or $M[Co(CN)_5NO]$ have failed, but invariably some other compounds with E.A.N. of 36 have appeared, either $M[Co(CO)_4]$ or $M_3[Co(CN)_6]$.

Complexes of Nickel

In all the complex cyanides of nickel the coordination number is four. No complex compound of the formula $M_2[Ni(CN)_6]$ in which the E.A.N. would be 36 has been prepared and it is hard to see why such a compound would not be stable.

TABLE 7

Complexes of Nickel

$M_2[Ni(CN)_4]$	28 − 2 + 8	34
$M_4[Ni(CN)_4]$*	28 + 0 + 8	36
$M_2[Ni(CN)_3NO]$	28 + 0 + 8	36
$Ni(CO)_4$		36

* W. M. Burgess: private advices.

The complex cyanide $M_2Ni(CN)_4$ obtained by treating salts of divalent nickel with excess alkali cyanide is not particularly stable. When the coordination number is four it is only possible for the nickel to show the E.A.N. of krypton when the nickel has the unexpected polar valence of zero. And we find that the complexes $[Ni(CN)_4]^{----}$ and $[Ni(CN)_3NO]^{--}$ exist as well as nickel carbonyl in which the polar valence is zero.

TABLE 8

Complexes of Manganese

$M_3[Mn(CN)_6]$	25 − 3 + 12	34
$M_4[Mn(CN)_6]$	25 − 2 + 12	35
$M_5[Mn(CN)_6]$	25 − 1 + 12	36
$M_3[Mn(CN)_5NO]$	25 − 1 + 12	36

The ordinary double cyanides obtained from salts of divalent and trivalent manganese and excess of alkali cyanide are not particularly stable, but the trend towards the E.A.N. of 36 is shown in the formation of complexes of monovalent manganese $[Mn(CN)_6]^{-----}$ and $[Mn(CN)_5NO]^{---}$. The E.A.N. influence must indeed be compelling to allow the existence of a complex ion with five charges.

Complexes of Chromium

The only complex cyanides of chromium on record are those formed from the common salts of divalent and trivalent chromium and excess of alkali cyanide

$M_3[Cr(CN)_6]$	24 − 3 + 12	33
$M_4[Cr(CN)_6]$	24 − 2 + 12	34

and neither of these are particularly stable.

With the coordination number of six in order to acquire the E.A.N. of krypton, chromium would have to show a polar valence of zero as it does in the hexacarbonyl, and we might look for the complex compounds $M_6[Cr(CN)_6]$, $M_5[Cr(CN)_5CO]$, $M_4[Cr(CN)_5NO]$. With coordination number four we might look for $[Cr(NO)_4]$ and $M_4[Cr(CO)_4]$ and with coordination number eight we might look for $M_4[Cr(CN)_8]$. As a matter of fact, molybdenum and tungsten do show the E.A.N. of xenon and radon, respectively, in the octacyanide complexes.

$M_4[Mo(CN)_8]$	42 − 4 + 16	54
$M_4[W(CN)_8]$	74 − 4 + 16	86

TABLE 9

Complexes of the Platinum Metals

$M_4[Ru(CN)_6]$	44 − 2 + 12	54	Xe
$M_2[Ru(CN)_5NO]$	44 − 2 + 12	54	Xe
$M_2[RuCl_5NO]$	44 − 2 + 12	54	Xe
$M_3Rh(CN)_6$	45 − 3 + 12	54	Xe
$M_2[PdCl_6]$	46 − 4 + 12	54	Xe
$M_2[Pd(CN)_4]$	46 − 2 + 8	52	
$M_2[OsCl_6]$	76 − 4 + 12	84	
$M_3[OsCl_6]$	76 − 3 + 12	85	
$M_2[OsCl_5NO]$	76 − 2 + 12	86	Rn
$M_4[Os(CN)_6]$	76 − 2 + 12	86	Rn
$M_3[Ir(CN)_6]$	77 − 3 + 12	86	Rn
$M_2[PtCl_6]$	78 − 4 + 12	86	Rn
$M_2[PtCl_2(CN)_4]$	78 − 4 + 12	86	Rn
$M_2[Pt(CN)_4]$	78 − 2 + 8	84	

Table 9 presents a representative although not a complete list of the complexes of the platinum metals, and it should be remembered that the discovery of these compounds was essentially accidental, and certainly not as the result of a deliberate attempt to confirm the E.A.N. doctrine. Again we find that the stabilizing effect of a coordinate layer of eight or twelve allows some complexes to exist with E.A.N. not that of an inert gas. But in the main, the tendency to acquire the E.A.N. of xenon and radon is very obvious and is controlling in every instance cited in which nitric oxide enters the complex.

Recent advices from W. C. Fernelius state that he has succeeded in preparing a compound of palladium, $K_4Pd(CN)_4$, in which palladium has the valence of zero and the E.A.N. of xenon. Fernelius applied the method by which Burgess obtained the similar nickel compound $K_4Ni\ (CN)_4$. A solution of potassium palladocyanide, $K_2Pd(CN)_4$, in liquid ammonia is treated with a solution of potassium in liquid ammonia. A sharp end point is reached both with the nickel and the palladium compound when the deep blue color of the potassium solution ceases to be discharged. It may be noted that when Burgess analyzed his preparation he was so astonished to find the composition $K_4Ni(CN)_4$ that he felt compelled to recheck his analyses before he could believe the existence of a compound in which nickel had a valence of zero. Comparison of this compound with the carbonyls, however, helped greatly to relieve the disbelief. On the other hand, Fernelius on the basis of Burgess' discovery hoped to prepare $K_4[Pd(CN)_4]$ and his success in doing so must be considered as a strong support of the potency of the effective atomic number.

SUMMARY

When the metal carbonyls were first discovered, their properties were startling because they seemed to violate nearly all the previously recognized generalizations of chemistry. Even to-day the existence of the carbonyls is not particularly emphasized in elementary courses of chemistry because it is rather hard to reconcile them with the first presentations of the generalizations of chemistry. Nevertheless, as the student progresses deeper into the knowledge of chemistry it becomes desirable to include the knowledge of the carbonyls both because they become more comprehensible when viewed in the light of Werner's system of coordination and because they themselves contribute to the comprehension of the Werner theory.

As long ago as 1931, Reiff in his discussion of cobalt nitrosyl carbonyl recognized the correlation between the effective atomic number and the volatility of carbonyls. A more recent study of *charged* Werner coordination complexes, that is, of complex ions, has shown a similar role of the effective atomic number.

We are standing on fairly firm ground when we point out the correlation between E.A.N. and the volatility of the carbonyl complexes and the existence of complex ions. Be it noted that we have made no postulates as to the arrangement of the electrons in quantum levels. In the inert gases the outer principal quantum group is supposed always to contain eight electrons. In the carbonyls and other Werner complexes there is no compelling reason to suppose that the electrons in the coordinating layer, be this layer of eight, ten, twelve or sixteen electrons, are not all at the same energy level.

Although we have confined our discussion almost exclusively to the property of volatility, the carbonyls are very interesting from the standpoint of several other properties, for example, magnetic susceptibility and dielectric constant. Enthusiasts in the interpretation of such properties try to draw conclusions as to the condition of the electrons, sometimes they become so dogmatic as to seem really to believe in the actual existence of the condition they postulate.

As Professor Smith said, "Theories come and theories go, but facts live on forever." The facts of chemistry are so multitudinous that we would be utterly helpless to use them had we not means of correlating them. Any postulates which reach beneath the surface of the directly observable to give a mechanism to correlate the facts are helpful. But a scientist without a sense of humor is pretty hopeless. Who in his right mind can regard as other than absurd the idea that an electron pair can simultaneously occupy positions in two atom shells to make up the supposedly necessary number in each atom? In fact, is not the electron itself a pretty ridiculous figment of the imagination? To be sure, we recognize the electron as a discrete entity with certain very definite properties, but in the light of comparison with any mechanism within our comprehension is not the electron perfectly impossible? By all means let us use a postulate which allows us to make a useful classification of facts, but never let us lose the sense to see how utterly ridiculous the postulate will look to one who has not like ourselves grown attached to it.

We do not expect ever to discover the ultimate reason for things, but we do expect ever to make progress in correlating and classifying the facts which we have already discovered and shall continue to discover. Dogmatic belief in ridiculous postulates retards this progress.

Since the foregoing manuscript was submitted the paper by Hieber and Lagally, *Zeit. Allgem. Anorg. Chem.*, 245: 321, November, 1940, has come to our attention in which the preparation of carbonyls of iridium by Hieber's high pressure technique is described. Non-volatile $[Ir(CO)_3]n$, corresponding to the cobalt tricarbonyl, is the principal product, but there is evidence that compounds corresponding to $[Co(CO)_4]_2$ and the volatile $HCo(CO)_4$ are also formed. A very volatile compound containing iridium is in evidence whenever traces of water or hydrogen are present in the autoclave, and although this compound can not be isolated for analysis it presumably is the carbonyl hydride $HIr(CO)_4$ in which iridium has the E.A.N. (86) of radon.

OBITUARY

WILLIAM FRANCIS GANONG

1864–1941

THE death of William Francis Ganong removes from the field of botany one of its outstanding leaders during the past fifty years. Dr. Ganong, a Canadian of loyalist descent, was born in St. John, New Brunswick, on February 19, 1864, the son of the late James H. and Susan E. Ganong. He was graduated from the University of New Brunswick with the degree of B.A. in 1884 and with that of M.A. in 1886, and in 1887 received his A.B. from Harvard. He obtained his Ph.D. from Munich in 1894, and in 1898 and 1920