TABLE I (*Concluded*)

Substance	Formula	B. p., °C.	Pressure, mm.	T, °K.	$m = T^2/20,000$	m from formula
Triethylphosphine........	$C_6H_{15}P$	128	760	401	8.0	8
Cacodyl..................	$C_4H_{12}As_2$	170	760	443	9.8	10
Zinc methyl..............	C_2H_6Zn	46	760	319	5.1	5
Mercury ethyl............	$C_4H_{10}Hg$	159	760	432	9.3	9
1,2,3,4-Tetrobromobutane.	$C_4H_6Br_4$	181	60	554	15.3	16
n-Octadecylene...........	$C_{18}H_{36}$	179	15	606	18.4	18
Bismuth triethyl..........	$C_6H_{15}Bi$	107	79	455	10.3	11
Carbon bisulfide..........	CS_2	46	760	319	5.1	5
Selenium tetrafluoride.....	SeF_4	100	760	373	6.9	7
Hydrogen telluride.......	H_2Te	0	760	273	3.7	4

Systematic deviations from Equation 2 are shown by some classes of presumably normal liquids: branched-chain, especially quaternary, hydrocarbons, and halogen derivatives with several halogen atoms attached to the same carbon atom, boil low; while cyclic compounds boil high.

Associated or polar liquids, as is well known, boil higher than would be expected from their nominal composition—the excess usually amounts to several units in m.

Summary

If T is the absolute boiling point at one atmosphere—or T_p the absolute boiling point at a pressure of p atmospheres—and m is the sum of the number of atoms of each element multiplied by one less than the number of the row of the periodic table in which it occurs, the relation

$$T \doteq T_p\,(1 - 0.2 \log_{10} p) \doteq \sqrt{20,000\ m} \qquad (2,3)$$

holds within a fraction of a unit of m for most normal organic liquids, and for many inorganic non-electrolytes.

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THE CONSTITUTION OF NICKEL CARBONYL AND THE NATURE OF SECONDARY VALENCE

BY ARTHUR A. BLANCHARD AND WILLIAM L. GILLILAND

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In its ease of formation from and dissociation into metallic nickel and carbon monoxide, nickel carbonyl strongly resembles the hydrates of salts. Hydrate formation is usually ascribed to a "secondary" valence of the constituents of the salt whose "primary" valence has already been engaged. In the case of nickel carbonyl, however, it would seem as if the secondary valence alone became engaged while the primary valences which both nickel and carbon monoxide are capable of developing remained dormant.

It is the purpose of this paper to present some experimental data[1] on which this view of the nature of nickel carbonyl is based and to offer a theory of the nature of "secondary" valence as displayed in this compound.

Nickel Carbonyl and Bromine

It was noted by Mond that bromine attacks nickel carbonyl liberating carbon monoxide;[2] and it was further found by Dewar and Jones[3] that the halogens reacted quantitatively with nickel carbonyl liberating carbon monoxide and yielding the nickelous halides. In our experiments nickel carbonyl and bromine were each dissolved in carbon tetrachloride, and the bromine solution was added gradually to that of nickel carbonyl. There appeared instantly a yellow precipitate of anhydrous nickel bromide, and a vigorous effervescence took place. Bromine was added until a further amount produced no more effervescence. When the nickel bromide had settled, the red color of excess bromine was visible. This and the solution were distilled off and the excess bromine was estimated: nickel carbonyl taken, 2.842 g.; bromine added, 4.032 g.; excess of bromine, 1.37 g.; amount entering reaction, 2.66 g.

The total gas evolved measured 1340 cc. reduced to standard conditions on the assumption that it was saturated with water vapor and carbon tetrachloride vapor at the room temperature, 23.5°. After sweeping the generator flask and connections with a part of this gas, 102.3 cc. was collected in a gas buret. When this was washed with 100 cc. of distilled water the volume was 100.8 cc. After treatment with 25 cc. of saturated barium hydroxide solution, which showed not the slightest trace of clouding, the volume remained 100.7 cc. Upon treatment with ammoniacal cuprous chloride the gas was rapidly absorbed, and a residue of 3.8 cc. was left which was doubtless air that had not been fully swept from the generating flask. The gas evolved, therefore, is pure carbon monoxide. Summing up we find the following amounts involved: nickel carbonyl, 2.84 g. or 0.0166 formula weight; bromine, 2.66 g. or 0.0166 formula weight; carbon monoxide, 1340 cc. or 0.060 formula weight. Since considerable over allowance was made for the vapor of carbon tetrachloride in the carbon monoxide, these results indicate that the reaction is quantitative: $Ni(CO)_4 + Br_2 \longrightarrow NiBr_2 + 4CO$.

Pure liquid bromine and nickel carbonyl react with explosive violence, but the diluted vapors, like the solutions in carbon tetrachloride, react quietly and completely. When gases, usually carbon monoxide, containing from 0.5 to 25% by volume of nickel carbonyl vapor, are treated with dil. aqueous bromine in a gas buret, the gas becomes filled with a dense white smoke (nickel bromide) and a considerable increase of volume is

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[1] A part of the Doctor's Research of Gilliland.

[2] Mond, *J. Chem. Soc.*, **57**, 749 (1900); **121**, 29 (1922).

[3] Dewar and Jones, *J. Chem. Soc.*, **85**, 203 (1904).

noted. After a short exposure to excess of bromine water no nickel carbonyl remains as shown by the very delicate test of introducing the gas at the base of a Bunsen burner. The slightest trace of nickel carbonyl will impart a peculiar grayish-blue, smoky appearance to the flame. With barium hydroxide the gases were shown to contain no trace of carbon dioxide.

This method is employed in subsequent work in estimating the amount of nickel carbonyl vapor in gas mixtures. According to the above reaction, one third of the increase of volume with bromine treatment gives the volume of nickel carbonyl vapor. In the subsequent determination of carbon monoxide, an amount equal to four-thirds of this increase should be subtracted from the total carbon monoxide to give the amount originally present.

Nickel Carbonyl and Sulfur

Nickel carbonyl reacts slowly with a solution of sulfur in organic solvents; a black precipitate is produced and a considerable amount of gas is evolved. Five g. of nickel carbonyl in 20 g. of chloroform and an excess of solid sulfur were sealed in a glass tube. Gas was withdrawn at intervals for a week and found to be nearly pure carbon monoxide. After an interval of more than two years, the tube was again opened; a trace of nickel carbonyl was still present and a considerable excess of sulfur. The black residue was extracted with chloroform and upon analysis was found to contain 54.09% of nickel (nickelous sulfide contains 64.66% of nickel; nickelic sulfide contains 55.5%).

A later experiment was made with about 1.5 g. of nickel carbonyl and 0.64 g. of sulfur in 19 cc. of chloroform with arrangements to draw off the gas continually into a receiver. The gas came off regularly for 36 hours, at the beginning at the rate of 35 cc. an hour. Due to errors of manipulation the total gas was not accurately determined, but it was within 25% of the amount demanded by the reaction $2Ni(CO)_4 + 3S \longrightarrow Ni_2S_3 + 8CO$.

The main reaction between nickel carbonyl and sulfur is certainly that expressed by the reaction just given but it cannot be claimed from the data that other reactions do not take place to some extent. The nature of this reaction is the same as that with bromine, namely, a non-metal combines with the nickel and the carbon monoxide is released. In this case the reaction is slow and is far from complete even after two years, whereas with bromine the reaction is complete and practically instantaneous. Approximately the same results with sulfur were found by Dewar and Jones.

Nickel Carbonyl and Oxygen

It has been repeatedly observed by all who have worked with nickel carbonyl that the pure substance or its solution in any of the solvents such as alcohol, acetone, chloroform, soon becomes cloudy when air and moisture both have access. Precipitates or crusts form which range in color from nearly black through brown and yellow-brown to light green, but a fine light green precipitate is the usual form which separates from solutions. Nickel carbonyl vapors react similarly in moist air, the interior of the container becoming coated with the fine, light green powder. A mixture of pure oxygen with nickel carbonyl vapors explodes with great violence and with extremely little provocation; great precaution should be observed in handling such gas mixtures.

Berthelot[4] analyzed the green powder obtained by the slow oxidation of nickel carbonyl covered with a layer of water and found the composition $C_2O_3Ni_3.10H_2O$. Lenher and Loos[5] arrived at the conclusion that the green precipitate was a compound of nickel carbonyl and nickel hydroxide with a composition varying around $Ni(CO)_4.Ni(OH)_2.4H_2O$—this, in spite of the fact that the precipitate dissolves entirely in dilute acids with an evolution of carbon dioxide and no slightest evidence of nickel carbonyl vapors. Thorne[5a] finds that the precipitate that slowly forms in a solution of nickel carbonyl in toluene to which air has access is basic carbonate of nickel.

Our own earlier qualitative observations upon the reactions of the substance indicated that it must be essentially a carbonate or a basic carbonate of nickel.

The oxidation product is insoluble in water and organic solvents but it dissolves quickly and completely in dilute acids, including acetic, with evolution of carbon dioxide. It is completely soluble in ammonium hydroxide.

When the oxidation product is heated in the air, it turns black and much odorless gas is evolved (as with nickel carbonate). Several samples that had been dried in a desiccator over sulfuric acid were analyzed for nickel by the dimethylglyoxime method with the following results.

Source of product	Nickel, %
No solvent: black scales formed inside a broken tube of pure nickel carbonyl	50.37
No solvent: green powder from box containing broken tube	49.28
Ether as solvent: blackened product (blackening accidental)	45.28
Acetone as solvent: green product	45.33
Another sample	44.83
No solvent: pure wet oxygen	45.14
Ethyl alcohol as solvent: green granules	44.46

A sample of oxidation product (0.7419 g.) was treated with dil. hydrochloric acid and the carbon dioxide measured and found to be 43.4 cc.

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[4] Berthelot, *Compt. rend.*, **113**, 679 (1891).

[5] Lenher and Loos, THIS JOURNAL, **22,** 114, 116 (1900).

[5a] Thorne, *J. Chem. Soc.*, **125**, 1967 (1924).

(reduced to standard conditions). This sample contained 45.6% of nickel. The oxidation product thus contains 0.297 formula weights of carbon dioxide per g. atom of nickel.

If the oxidation product is carbonate or basic carbonate it should, when heated out of contact with air, give off only carbon dioxide and water vapor and leave a residue of pure nickelous oxide. Actual experiments gave a residue containing more nickel than corresponds to the formula NiO (about 90.4% of NiO and 9.6% of Ni) and a gas containing mainly carbon dioxide but also small amounts of carbon monoxide and hydrogen.

Pure nickel formate evolves carbon dioxide, carbon monoxide and hydrogen as if the decomposition were taking place by both of the following reactions: $Ni(HCOO)_2 \longrightarrow Ni + 2CO_2 + H_2$; $Ni(HCOO)_2 \longrightarrow Ni + H_2O + CO_2 + CO$.

A mixture of nickel carbonate with a small amount of formate would give about the results given by our oxidation product, because the carbon monoxide and hydrogen would for the most part be oxidized by the nickel oxide left by the decomposition of the carbonate.

Direct experiments were, therefore, tried to show the presence of formic acid in the oxidation product. One sample was tested qualitatively by the method described by Mulliken.[6] It was dissolved in a slight excess of acetic acid and the solution was digested at 50° with mercuric oxide. The excess of mercuric oxide was filtered off, the filtrate was cooled and lustrous white crystals of mercuric acetate and mercuric formate separated. The crystals were collected on a filter, then washed with some water into a test-tube and boiled, whereupon a characteristic dark gray precipitate of free mercury appeared, collecting soon into a small globule of mercury. The same result was obtained with a known mixture of nickel carbonate and formate but not with carbonate alone.

After practicing with a known solution of formic acid and with an inferior sample of oxidation product, the following experiment was tried with a sample of 2.00 g. of oxidation product: 25 cc. of water and 25 cc. of 6 *N* sulfuric acid were added; the mixture was warmed to 60° and all carbon dioxide blown out of the distilling flask. It was then distilled, 43 cc. in all being driven over, until the last portion of 5 cc. neutralized not more than a drop of *N* sodium hydroxide solution. In all, the distillate neutralized 1.24 cc. of *N* alkali. The neutralized distillate was evaporated to dryness in a small test-tube; 10 cc. of cold concd. sulfuric acid was added and the tube was connected with a gas buret. On warming, 15.6 cc. of gas was evolved. Of this, the first part was used for sweeping the connections and the second part was tested: with barium hydroxide solution it diminished 0.1% in volume and showed the barest turbidity ($BaSO_4$ or

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[6] Mulliken, "Methods for the Identification of Pure Organic Compounds," Wiley and Sons, **1904**, vol. 1, p. 83.

$BaSO_3$). With cuprous chloride two-thirds was absorbed, which in view of the inadequate sweeping indicates that the gas is all carbon monoxide.

This sample of the oxidation product contained 45.6% of nickel. Assuming that the 15.66 cc. of gas (standard conditions) was all carbon monoxide and that this is a measure of the formate, we find 0.045 formula weight of formate radical per gram atomic weight of nickel. If on the other hand we assume that the 1.24 cc. of N sodium hydroxide solution represents the formic acid distilled, we have 0.080 formula weight of formic acid per gram atomic weight of nickel. The latter value is probably more nearly the true one.

This sample of the oxidation product may, therefore, be considered as containing 29.7 equivalents of carbonate, 4.0 equivalents of formate and 66.3 equivalents of hydroxide of nickel.

In all attempts to prepare the oxidation product the yield was very small; also, in all the preliminary attempts to isolate the gaseous products of the oxidation reaction, there was a seemingly mysterious disappearance of material. Nickel carbonyl has a very high vapor pressure and it is somewhat soluble in water. It escapes by diffusion through the water seals of the apparatus. According to the method finally adopted, a glass vessel of about 150 cc. capacity with stopcocks at both ends was filled with oxygen; a few cubic centimeters of water and about 2 g. of nickel carbonyl were forced in, then mercury was quickly blown in until it stood in the capillary tubes to a distance about 2.5 cm. above each stopcock. A very rapid rise in pressure due to the evaporation of nickel carbonyl was shown on the manometer. After about half an hour it was estimated that the gas had become saturated with nickel carbonyl vapor. The pressure reading then was 1011 mm. After 48 hours the pressure had risen to 1342 mm. and most of the liquid carbonyl had changed to a flocculent green powder. The gas was then drawn off through a spiral condenser tube immersed in a freezing mixture. About 50 cc. of the gas was used to sweep the condenser and connection and then a sample was taken for analysis; a large diminution of volume was noted due to the condensing of the nickel carbonyl by the freezing bath.

The experiment was repeated, filling the apparatus of 128 cc. capacity with oxygen of 88% purity and then forcing in from one end about 1.8 g. of nickel carbonyl and about 3 cc. of water. The other stopcock was left open for a few minutes to allow the escape of gas forced out by vaporization of the nickel carbonyl; then the stopcocks were sealed with mercury and closed. The pressure rose rapidly at first, then more and more slowly. After 64 days the pressure had increased to considerably more than two atmospheres. The gas was drawn off through a spiral condenser immersed in ether and carbon dioxide snow, 58.8 cc. being used to sweep the connections and 80.4 cc. being taken for analysis. The 139.2 cc. drawn off was measured after the nickel carbonyl had been condensed; the gas left in the reaction vessel under atmospheric pressure was still saturated with nickel carbonyl. The analyses of the gas from the two experiments follow.

	Expt. 1, cc.	Expt. 2, cc.
Sample	31.5	80.4
After treatment with Br_2	39.6	81.0
After treatment with NaOH	..	81.0
After treatment with pyrogallate	26.7	63.8
Residue after acid CuCl	4.8	7.1

The following volumes and percentages are calculated.

	Volume, cc.	%	Volume, cc.	%
$Ni(CO)_4$	2.7	8.6	0.2	0.25
O_2	12.9	41.0	17.2	21.4
Total CO	21.9	..	56.7	..
Net CO	11.1	35.2	55.9	69.5
Residue	4.8	15.2	7.1	8.8

The oxidation product within the reaction tube was of the usual appearance and had become somewhat caked together through long standing. To clean it out after the last experiment a little dil. hydrochloric acid was introduced and to our great surprise the solid dissolved quickly and completely but without the slightest trace of effervescence. All the other samples prepared by us had been obtained through long exposure to atmospheric air and it must be that the carbonate in them had come from the carbon dioxide of the air rather than from oxidation of the nickel carbonyl.

The reaction of nickel carbonyl with oxygen thus appears to be of the same nature as that with bromine and sulfur, namely, the nickel is oxidized and carbon monoxide is set free. In this case, however, a small fraction of the carbon monoxide, apparently independently of the oxidation of the nickel, undergoes the unusual change into formic acid. Except in the presence of strong bases and at elevated temperature carbon monoxide does not ordinarily combine with water to yield formic acid.

The reactions of nickel carbonyl with the non-metals bromine, sulfur and oxygen, and doubtless with non-metals in general, are essentially the same as if the nickel alone combined with these elements. The carbonyl groups are released from combination and escape as free carbon monoxide.

The Reaction of Nickel Carbonyl with Grignard Reagents

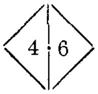
The experimental details of this part of the investigation are presented in another paper.[7] It is well known that carbon monoxide alone is without reaction with most Grignard reagents; in combination with nickel in nickel carbonyl, however, it reacts very vigorously, with the formation of a series of products which might be predicted if carbon monoxide were to react at all; free metallic nickel is left when the carbonyl group thus reacts.

[7] This Journal, **48**, 410 (1926).

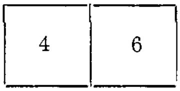
Structure of Nickel Carbonyl

It is apparent from the foregoing experimental work that nickel carbonyl is a loose association of nickel and carbon monoxide, for not only is the compound easily formed and dissociated, but either constituent reacts alone with substances with which it would be expected to react were it in the free state, leaving the other constituent uncombined. In no case is nickel carbonyl known to enter a metathetical reaction with another compound.

If there is a clear boundary between primary and secondary valence it ought to be possible to define the difference in terms of the electron arrangement. With this end in view we have tried to construct the most probable arrangement of the electrons in nickel carbonyl. It was first suggested by Langmuir[8] that the metal atoms in the carbonyls[9] $Ni(CO)_4$, $Fe(CO)_5$, $Mo(CO)_6$, possess sheaths of 18 electrons. Thus, according to Bury's notation[10] the electrons of the nickel atom would fall in layers 2-8-8-18. The kernel charge of (Ni_{26} 2-8-8) is 10 and would balance 10 electrons of the sheath leaving the other eight to the kernels of the carbonyl groups. Langmuir[11] attributes the remarkable stability of carbon monoxide to an electronic arrangement like that of nitrogen. Pease[12] holds that nitrogen and carbon monoxide as well as acetylene all have the triple bond, and G. N. Lewis[13] holds that all of these as well as the cyanide ion possess what with certain reservations he describes as a triple bond. This bond in carbon monoxide may be represented in the plane diagram I,



I



II

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[8] Langmuir, *Science*, N. S. **44**, 64 (1921).

[9] Mond in his last publication [*J. Chem. Soc.*, **121**, 29 (1922)] gives the analysis of molybdenum carbonyl as $Mo_5(CO)_{26}$ instead of $Mo(CO)_6$ as in his earlier work [*ibid.*, **97**, 798 (1910)]. In view of the very small amount of substance that he had for analysis, too much reliance cannot be placed on his values and we choose to regard his earlier formula as more probable, first, because the compound is distinctly volatile, Mond having purified it by sublimation (it sublimes at 30° to 40° in an atmosphere of carbon monoxide or of hydrogen) and a substance of the complicated formula would be unlikely to be volatile; second, by the method of analysis the entire molybdenum would be found and appear in the final figure, whereas the methods of estimating carbon monoxide by heating and by treating the substance with bromine and measuring the volume of gas might easily show a little less than the true amount. Molybdenum carbonyl is said by Mond to begin to decompose at 150°.

[10] Bury, THIS JOURNAL, **43**, 1602 (1921).

[11] Langmuir, *ibid.*, **41**, 903 (1919).

[12] Pease, *ibid.*, **43**, 991 (1921).

[13] Lewis, "Valence and the Structure of Atoms and Molecules," A. C. S. Monograph Series, Chemical Catalog Co., **1923**, p. 126.

in which the corners and the dot in the center represent the projections of electron pairs of the sheaths and the numerals show the kernel charges. With two more electrons the octets can be completed with but two pairs of electrons held in common and we have the carbonyl group as in Diagram II. But this group is not a neutral molecule like carbon monoxide. If it is not to exist as a negative ion some of the electrons must be shared with other atoms. According to our structure of nickel carbonyl, four electrons of each carbonyl group are held in the sheath of the nickel atom and 16 of the nickel sheath are shared, leaving two which are put in the polar axis unshared.

The diagrams represent what seems to us the most probable structure of nickel carbonyl as well as of the other very volatile carbonyls.

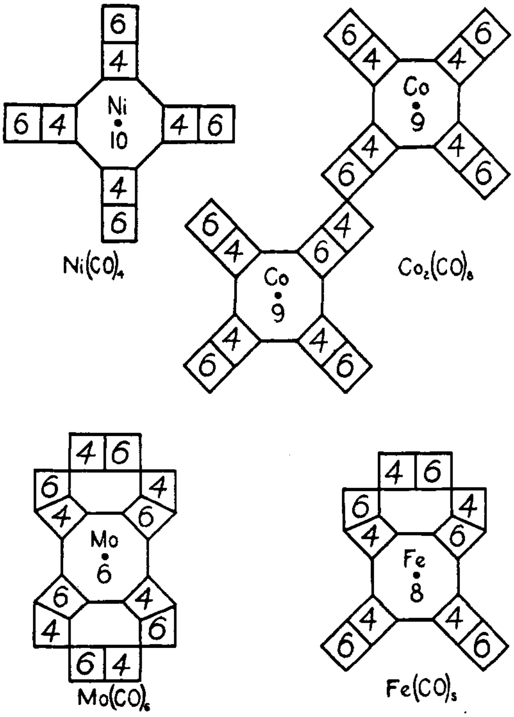

Fig. 1.—The dot in the center of the octagons is the projection of the pair of electrons in the polar axis. The corners are the projections of the eight lateral pairs of electrons of the sheath of eighteen. The numerals are the kernel charges. In each of these cases the total number of electrons is equal to the sum of the kernel charges, and an electrostatically self-contained structure is thus achieved.

The kernels of the metal atoms are as in the parentheses: (Fe_{26} 2-8-8) 18, (Co_{27} 2-8-8) 18, (Ni_{28} 2-8-8) 18, (Mo_{42} 2-8-18-8) 18, which leaves consistently sheaths of 18 electrons, the 8 lateral pairs of which are shared with the carbonyl groups. The octets of the latter are completed when necessary by their corners swinging together to share a pair. Such electrostatically self-contained structures can account for the volatility of these heavy complex molecules.

The strongest argument in favor of this structure is that it gives consistently the same configuration of electrons in all the carbonyls which possess an astonishingly high volatility. The outer layer of the kernel is 8, a remarkably stable group, and the group of 18 is in itself inclined to be stable although not in a sheath unless it is stabilized by being shared with exterior kernels. The two unshared electrons in the polar axis might be assigned to the kernel but then the argument that layers of 8 and 18 are particularly stable would be lost.

It is true that there are other carbonyls with lesser numbers of carbonyl groups, as well as the hydrated carbonyl of cuprous chloride but in none of these is the symmetrical structure of the layer of 18 attained and the electrostatic stray field resulting from the lesser symmetry accounts for the low volatility.

The electronic structure of krypton, 2-8-18-8, has been thought by some[14] to be indicated by the diamagnetic properties of nickel carbonyl as well as of a number of complex salts. But it is to be noted that the kernel (Ni_{28} 2-8-18) of such a structure is electrically neutral. It would have no electrostatic attraction for the 8 sheath electrons. Important as the magnetic properties of the electrons, or the electron orbits, are in the structural forces of molecules, it is difficult to believe that magnetic forces alone could hold a complete outer layer of 8.

We believe that in general the maximum number of electrons possible at the succeeding levels is 2, 8, 18, 32, respectively, and that the outer layer, or sheath, tends to collect 8 electrons, but can only support more than 8 when aided by the + charges of surrounding atom kernels. We prefer to think of the position of electrons held in common as fixed. If they describe orbits, their centers of electrostatic attraction must lie at points between the two atom nuclei. In some cases they probably describe double loops or figures 8 about the two nuclei, in which case the point of intersection would approximate the center of attraction, or the static position. Such a figure 8 orbit may easily degenerate into a vibration in a plane between the two nuclei and perpendicular to a line connecting them.[15] In choosing the probable position of electrons in compounds, Coulomb's law of electrostatic attraction and repulsion, subject of course to the requirements of the energy levels, should be the guiding principle.

Secondary valence is a term that is used in a vague way to indicate the nature of the forces which bind together molecules in which the primary valences are satisfied, particularly in the cases when an ordinary valence cannot still be assigned to each atom through a rearranging of the bonds. Whether our proposed structure of nickel carbonyl or some other is better, it is certain that the formation of this compound is due to the rearrangement of electrons into layers which give greater stability. But this is precisely the cause of primary valence. The layers involved in primary valence usually become octets; those involved in secondary valence are often larger than octets, but the distinction is not universal enough to serve as a means of classification.

[14] See, for example, Welo and Baudisch, *Nature*, **116**, 606 (1925).

[15] Main Smith, "Chemistry and Atomic Structure," D. Van Nostrand Co., **1924**, p. 203.

Space does not allow a careful marshaling of cases of clear primary valence and clear secondary valence and of cases like this one of nickel carbonyl which has some characteristics of both kinds of valence. Suffice it to say, that using the term in the vague sense that describes only the general nature of the substance and not its precise structure, nickel carbonyl is properly classified as a secondary valence compound. The only way in which valence may be precisely defined is by stating the kernel charge, the number of electrons in the sheath and the number held in common with other atoms. When this is guesswork, the valence itself is guesswork. Guesses of this kind are justifiable when they lead ultimately to a satisfactory system of classification.

Summary

Experimental data concerning the reaction of nickel carbonyl with the non-metals bromine, sulfur, oxygen and with the Grignard reagent are given.

The data support the claim that nickel carbonyl is a compound in which secondary valence alone is exerted, either constituent being free to enter into its ordinary reactions, the other constituent being thereby left alone in its ordinary free condition.

A structure of the extremely volatile carbonyls is proposed which would give a very small stray electrostatic field; the sheath of the metal atom contains 18 electrons in each case.

An interesting case of the formation of formic acid in small amount from carbon monoxide and water during the slow oxidation of nickel carbonyl is incidentally brought to light.

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VELOCITY—TEMPERATURE COEFFICIENT IN LIQUID MEDIA

BY HARRY ESSEX AND OTTO GELORMINI

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The measurements to be found in the literature on the velocity of strictly homogeneous, isolated reactions both in the gaseous state and in liquid media, show in the majority of cases that the effect of temperature is given within the experimental error of the measurements by the relation, $\mathrm{d}\, ln\, k/\mathrm{d}T = E/RT^2$, in which E is a constant characteristic of the reaction and the medium.

This is the relation originally proposed by Arrhenius and shown by him to be a consequence of his theory of the active-passive molecule equilibrium and of other postulates so improbable that the equation has until recent years been considered empirical. However, in the recent intensive application of the kinetic theory, the distribution law and the quantum hy-