LIV.—*Some New Metallic Carbonyls.*

By the late LUDWIG MOND, F.R.S., HEINRICH HIRTZ, and MATTHEWMAN DALTON COWAP.

Introduction by Robert Ludwig Mond.

MY father, the late Dr. Ludwig Mond, had his attention drawn to the possible existence of compounds of carbon monoxide and various metals by the examination of a peculiar black deposit, which had formed on some nickel valves used in his ammonia-soda process, which he described in his Presidential Address to the Chemical Section of the British Association in 1896. The examination of this black compound (a carbide of nickel), which was conducted in his private research laboratory by his assistants, Dr. Carl Langer and Dr. Friedrich Quincke, led to the discovery of a volatile compound of nickel and carbon monoxide, the properties of which were described in 1890 (Trans., **57**, 749). Further research led to the discovery of ferropentacarbonyl and diferroheptacarbonyl (Mond and Langer, Trans., 1891, **59**, 1090), and although numerous experiments were made to obtain similar compounds with other metals, they led at that time to no success.

The study of these compounds and the technical application of the nickel carbonyl process monopolised the time of Dr. Mond and his staff to the exclusion of further scientific research in this direction.

The low-temperature research work carried on by Sir James Dewar at the Royal Institution, in which Dr. Mond took a very great interest, led him to suggest to Sir James Dewar to examine the action of carbon monoxide on nickel at high pressures. The result of this work is embodied in a patent taken out by Sir James Dewar on behalf of my father in 1902, and the comparative facility with which the reaction proceeded at a higher pressure led my father to instal a high-pressure plant at his private laboratory for the further study of this problem. On the conclusion of the experiments for obtaining the technical data of a high-pressure process, he directed his attention once more to studying the behaviour of other metals when subjected to the action of carbon monoxide under these high pressures, and it was chiefly to this research that he devoted the time and thought he could afford for scientific research during the latter years of his life.

The present paper was drawn up on Dr. Mond's instructions to be read before the Chemical Society, and although he did not see it in its finally revised form, he was fully conversant with all the experiments and the results obtained. The actual researches presented great difficulties, both of a technical and theoretical nature, and were very ably carried out by my father's assistants, Dr. Heinrich Hirtz and M. Dalton Cowap, acting under my father's instructions, or my own when my father was absent.

R. L. M.

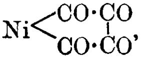
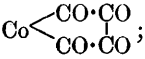
The following table gives a résumé of the present state of knowledge of the different compounds of the metals with carbon monoxide.

All these carbonyls have very similar chemical properties; thus, when heated, they all decompose into carbon monoxide and the metal, which is deposited in the form of a bright metallic mirror. They are not attacked by non-oxidising acids, but are quickly dissolved by oxidising acids, and especially by aqueous solutions of the halogens, with the evolution of carbon monoxide. At least one of the carbonyls of each metal is volatile without decomposition, and can be purified by distillation or sublimation. They are all more or less soluble in the usual organic solvents, such as ether, ethyl alcohol, benzene, oils, etc., and are all insoluble in water.

Table of Physical and Chemical Properties of Carbonyls.

	Formula.		Sp. gr.	Melting point.	Boiling point.	Vapour pressure.	Colour.	Formation.	Decomposition.
	Empirical.	Molecular.							
Ni.	$Ni(CO)_4$	$Ni(CO)_4$	1·32446 at 14°	−25°	+43°/751 mm.	238 mm. at 15°	Colourless liquid	Ni and CO at ordinary pressure.	To Ni and CO (partial) at 0° in a vacuum and at 50° under ordinary pressure; no intermediate products could be found.
Co.	$Co(CO)_4$	$Co_2(CO)_8$	1·73	+51°	Decomposes above 52°	0·072 mm. at 15°	Orange crystals	Co and CO at min. of 40 atm. and 150°.	To Co and CO (complete) above 60°; to $Co(CO)_3$ and CO between 50° and 60°. No recombination at 0—60°.
	$Co(CO)_3$	?	?	Decomposed above 60°		—	Black crystals	From $Co(CO)_4$ at 60°.	To Co and CO above 60°; no intermediate products could be found.
Fe	$Fe(CO)_5$	$Fe(CO)_5$	1·4664 at 18°	−21°	102·8°/749 mm.	25·9 mm. at 16·1°	Yellow liquid	Fe and CO at high pressure and temp. From $Fe_2(CO)_9$ by distilling in CO.	To $Fe_2(CO)_9$ and CO by light; to Fe and CO by heating vapours.
	$Fe_2(CO)_9$	?	2·085 at 18°	Decomposed at 100°		Not measurable	Gold coloured crystals	$Fe(CO)_5$ by light. From Fe and CO by light.	To $Fe(CO)_5$ and CO and Fe by heating to 100°; to $Fe(CO)_4$ and $Fe(CO)_5$ by heating solution to 95°.
	$Fe(CO)_4$	Very high	1·996 at 18°	Decomposed at 140—150°		—	Green crystals	From $Fe_2(CO)_9$ by heating in solution at 95°.	To Fe and CO by heating to 150° or above. No recombination to $Fe(CO)_5$ or $Fe_2(CO)_9$ by CO; pressure up to 150 atm.
Mo.	$Mo(CO)_6$	?	1·96 at 15°	Volatilises before melting		?	White crystals	Mo and CO at a minimum of 130 atm. and 200°.	To Mo and CO by heating to above 150°.
Ru.	?		?	?	?	?	Rose to orange	Ru and CO at a minimum of 400 atm. and 300°.	To Ru and CO by heating.

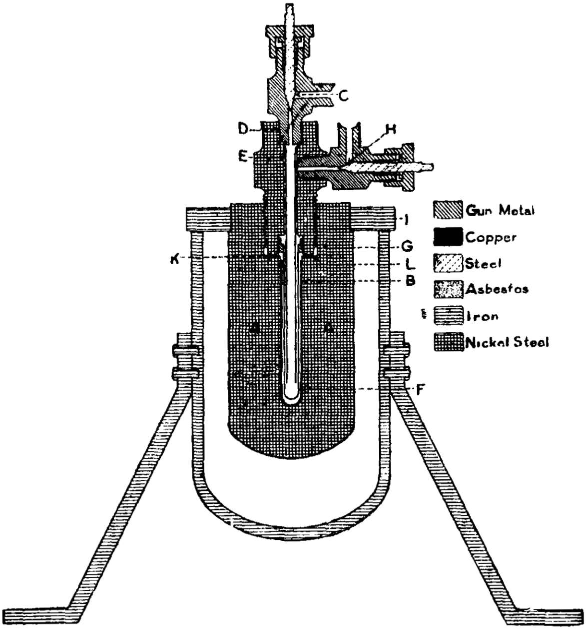
"Action of carbon monoxide on nickel" (Mond, Langer, and Quincke, Trans., 1890, **57**, 749); "Studi sul nichel tetracarbonile" (Mond and Nasini, *Atti R. Accad. Lincei*, 1890, **7**, i, 411); "Ueber einige physikalische Eigenschaften des Nickel-tetra-karbonyls" (Mond and Nasini, *Zeitsch. physikal. Chem.*, 1891, **8**, 150); "On nickel carbon oxide and its application in arts and manufactures" (Mond, *Brit. Assoc. Rep.*, 1891); "Metallic carbonyls" (Mond, *Roy. Inst. Lecture*, June 3rd, 1892); "The history of my process of nickel extraction" (Mond, *J. Soc. Chem. Ind.*, 1895, **14**, 945); "The extraction of nickel from its ores by the Mond process" (Roberts-Austen, *Proc. Inst. Civil Eng.*, 1898—1899, **135**, Pt. I); "Ueber die chemische Dynamik des Nickelkohlenoxyds" (Mittasch, *Zeitsch. physikal. Chem.*, 1902, **40**, 1); "Einige Beobachtungen über Losungsvermögen und elektrische Leitfähigkeit von flüssigem Nickelkohlenoxyd" (Mittasch, *ibid.*, 1903, **46**, 37); "Some physical properties of nickel carbonyl" (Dewar and Jones, *Proc. Roy. Soc.*, 1903, **71**, 427); "The toxicology of nickel carbonyl" (Armit, *J. Hygiene*, 1907, **7**, 525); "Note on a volatile compound of cobalt with carbon monoxide" (Mond, Hirtz, and Cowap, *Brit. Assoc. Rep.*, 1908; *Chem. News*, 1908, **98**, 165); "Ueber eine flüchtige Verbindung des Eisens mit Kohlenoxyd" (Mond and Quincke, *Ber.*, 1891, **24**, 2248); "Note on a volatile compound of iron with carbonic oxide" (Mond and Quincke, Trans., 1891, **59**, 604); "On iron carbonyls" (Mond and Langer, *J. Soc. Chem. Ind.*, 1891, **10**, 1090); "The physical and chemical properties of iron carbonyl" (Dewar and Jones, *Proc. Roy. Soc.*, 1905, *A*, **76**, 558); "On a new iron carbonyl, and on the action of light and of heat on the iron carbonyls" (*ibid.*, 1907, *A*, **79**, 66).

The physical properties, however, vary very considerably, from nickel tetracarbonyl, a liquid which is very easily volatile and has a specific gravity of 1·32, to the non-volatile diferrononacarbonyl, with a specific gravity of 2·085. Some can be obtained in the form of gas, liquid, or solid; others as a solid and gas; and others still only in the solid state. The colour varies from black to white through almost the whole spectrum. Owing to the various composition of these compounds, it is extremely difficult to construct a general chemical formula for them, but as they have such a similar chemical behaviour they must be constituted in a similar manner. One cannot regard all the carbonyl groups as being combined directly with the metal, as that would involve cobalt being sexa- and octa-valent, iron octa-, nona-, and deca-valent, and so on. Also, ring-formation, as hitherto supposed, does not explain all the properties; for instance, if nickel carbonyl has the constitution  $\mathrm{Ni}<\begin{array}{l}\mathrm{CO\cdot CO}\\ \qquad | \\ \mathrm{CO\cdot CO}\end{array}$, cobalt tetracarbonyl should have a similar constitution, namely,  $\mathrm{Co}<\begin{array}{l}\mathrm{CO\cdot CO}\\ \qquad | \\ \mathrm{CO\cdot CO}\end{array}$; but in this case it is difficult to understand why it has double the molecular weight in benzene solution, and, moreover, such a constitution does not explain why one carbonyl group should be more easily eliminated than the rest. Further, diferrononacarbonyl cannot thus be brought into line with the other carbonyl compounds. In the case of molybdenum carbonyl one would have to assume the formation of a ring containing seven atoms, which can be formed only with great difficulty among organic compounds. Consequently, we are at present of the opinion that these compounds have a molecular rather than an atomic constitution, similar to the hydrates of salts or of acids, the carbonyl group taking the place of the water of crystallisation or hydration. Here again, however, the difficulty arises that we have to assume that these compounds, although they can be obtained in a gaseous form, and so far as they could be investigated therein, have a normal gas density, exist in the gaseous state also in this molecular condition. This would be quite an unusual property, but, in our opinion, not more difficult to assume than the fact that many organic compounds have, at a temperature slightly above their boiling points, an abnormally high vapour density, and also that gaseous sulphur exists in the form of S_8, S_6, and S_2, according to the temperature and pressure.

EXPERIMENTAL.

In a previous paper read before the British Association and published in the *Chemical News* of October 2nd, 1908, we have described the formation of a cobalt carbonyl, and at the International Congress of Applied Chemistry, London, 1909, Dr. Mond, in his Presidential Address to Section II, announced the formation of a new cobalt carbonyl and also the formation of a molybdenum and ruthenium carbonyl. We now give some further details on the formation and properties of these compounds.

FIG. 1.



The apparatus which we used for these experiments consisted of a nickel-steel tube, which could be heated up to 450° and subjected to a pressure of upwards of 500 atmospheres. The details of the construction of this retort are shown in Fig. 1. *A* represents the retort, which is copper-lined at *B* so as to prevent the carbon monoxide from attacking the iron of the retort. The gas enters the retort at the pressure valve *C*, fixed to the retort by a cone-joint *D*. Brazed into the bottom part of the joint *D* is a copper tube *E*, which reaches to the bottom of the retort. The gas penetrates through the material, which is contained in a glass tube *F*, this tube being loosely held in the top of the retort by a gun-metal nipple *G*. The gas then leaves the retort at the outlet valve *H*. The cover, together with the copper and glass tube, is screwed into the body of the retort at *I*, and the joint is made by a metal ridge *K*, which protrudes from the bottom part of the screw *I*. It was found necesary to add a copper washer *L*. With this arrangement the retorts could be kept tight up to 500 atmospheres' pressure and a varying temperature up to 450°. The carbon monoxide was compressed by a two-stage compressor into a cylinder, from which it was taken to the inlet valves of the retorts; the gases were then led through the retort, and from the exit they passed through a glass tube, cooled in a freezing mixture, and then through another glass tube, heated so that a metallic mirror could, if possible, be formed, which could then be analysed.

Cobalt Carbonyl.

The preparation of cobalt carbonyl, $Co(CO)_4$, was carried out by the following method. Cobalt oxalate was carefully heated until it was completely converted into oxide. This was thoroughly washed free from chlorides, which we found to be detrimental to the formation of the carbonyl. The oxide was then dried at about 120°, filled into the glass tube of the retort, and the whole apparatus was screwed together. The cobalt oxide was reduced to cobalt by a current of hydrogen at 300° under 5 atmospheres' pressure, and, after reduction, the hydrogen was displaced by carbon monoxide and the temperature lowered, whilst the pressure was increased. The minimum pressure necessary for the formation of cobalt carbonyl was found to be between 30 and 40 atmospheres at a temperature of about 150°. The higher the pressure the more rapid is the formation of the carbonyl, but we are not as yet prepared to say how far the pressure may be raised. We have prepared cobalt carbonyl under 30, 50, 100, 200, and 250 atmospheres' pressure, and at a temperature varying with the pressure from 150° to 220°, obtaining fine orange-coloured, transparent crystals of the composition $Co(CO)_4$. Some of the properties have been described already in the above-mentioned paper. We repeat these here with some corrections and additions. The crystals are best preserved by sealing them in a glass tube in an atmosphere of hydrogen or carbon monoxide. When they are left in contact with the atmosphere, decomposition takes place, a deep violet substance consisting of a basic cobalt carbonate being left behind. Cobalt carbonyl is very slowly attacked by non-oxidising acids, such as hydrochloric or sulphuric, whereas when nitric acid or bromine is present, the reaction is accelerated considerably, and the corresponding cobalt salt is formed with the elimination of carbon monoxide, according to the equation $Co(CO)_4 + Br_2 = CoBr_2 + 4CO$. Cobalt carbonyl is insoluble in water, but more or less soluble in organic solvents, such as carbon disulphide, ether, naphtha, alcohol, and also in nickel carbonyl. If these solutions are kept for some time, or if they are warmed, decomposition ensues.

The specific gravity measured by the suspension method at 18° is 1·73, but we do not yet regard this figure as final, for, if the substance is kept only for a few hours, the specific gravity increases considerably, owing to decomposition. The molecular formula was determined by the cryoscopic method, which gave the molecular weight of 328, corresponding practically with $Co_2(CO)_8$. The vapour pressure could not be directly measured owing to decomposition; we therefore employed a method by which it was possible to estimate it as follows. Pure carbon monoxide was passed over the crystals at a rate of about half a litre per hour at a temperature of 23—25°. The gas volatilised the crystals to a certain point, and this partly saturated gas was passed through a coil which was kept exactly at 15°. The excess of cobalt carbonyl which the gas had absorbed at 23—25° over that which it could keep in a gaseous state at 15° was deposited in the cooling coil in the form of fine crystals, so that the gas leaving the coil was quite saturated at 15°. Care was taken that the room-temperature was well above 15° during the experiment. The carbon monoxide, saturated with gaseous cobalt carbonyl, was now passed through bromine-water in a series of absorption bulbs, and the cobalt retained by the bromine-water was estimated by analysis. It was found that 42·58 litres of carbon monoxide had taken up 10·6 milligrams of cobalt or 4·01 c.c. of cobalt carbonyl vapour, corresponding with 0·0944 c.c. per litre (0·0094 per cent. by volume). This corresponds with a vapour pressure of 0·072 mm. at 15°. This low value is very remarkable, as the vapour pressure of nickel carbonyl under these conditions is about 200 mm.

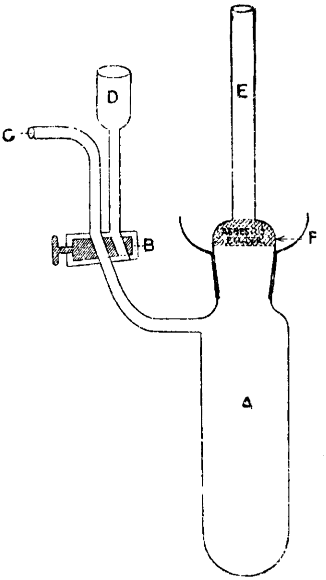
The pure crystals melt, without decomposing, at 51°. Very slow decomposition sets in immediately after melting, and the decomposition is quite appreciable at 53°. At 60° the decomposition is fairly rapid, so that the compound is entirely decomposed at this temperature in about two working days. It was found that exactly one-quarter of the carbon monoxide present in the carbonyl was eliminated, as is shown in the following table:

$Co(CO)_4$ taken (milligrams).	Co found (milligrams).	CO (A) given off at 60° (milligrams).	CO (B) in compound (milligrams).	CO/Co in molecular proportion.	B/A.
239·0	82·3	38·8	—	1·006	—
154·4	53·3	25·2	—	1·003	—
calculated					
141·0	—	23·4	93·0	—	3·98

The amount of gas given off was measured at short intervals, and a curve (see Fig. 3) was drawn showing the rate of decomposition of cobalt carbonyl at 60°. From this curve we conclude that there is no further stage of decomposition between the compound $Co(CO)_4$ and the compound $Co(CO)_3$.

The new compound, *cobalt tricarbonyl*, $Co(CO)_3$, was purified and analysed as follows. It was dissolved in warm benzene, and, on cooling the solution, the substance separated in jet black crystals. These were collected, dried, and decomposed with bromine-water. The carbon monoxide evolved and the cobalt remaining were estimated by the usual methods. It was extremely difficult to obtain this compound sufficiently pure for analysis, as it is so very easily changed in air.

Fig. 2.



The apparatus used for this analysis is shown in Fig. 2. *A* is the crystallisation and decomposition vessel. It is connected at one side with a two-way cock *B*. Through *C* an inert gas, such as hydrogen or carbon dioxide, could be passed through it, and at *D* the bromine-water could be added. On the top was ground in another tube *E*, which could be fitted with an asbestos filter *F*. The two-way cock and the top tube were fitted with a mercury seal, so that a complete vacuum could be obtained. The cobalt tetracarbonyl was then decomposed in a separate vessel at 60°. The residue was dissolved in warm benzene in an atmosphere of hydrogen and filtered into the vessel *A*, tube *E* being meanwhile removed. The filter was composed of asbestos-wool contained in a dropping funnel, in which an atmosphere of an inert gas was maintained. During filtration and crystallisation a current of inert gas was passed through the apparatus. When the warm benzene solution was in the vessel, the apparatus was cooled in ice-water until all the benzene was frozen. Tube *E* was now inserted, the apparatus reversed, the benzene slowly thawed, and passed through the filter. The crystals of cobalt tricarbonyl remained in *A* or at *F*. Dry inert gas was now passed through the apparatus at the ordinary temperature until the crystals were quite dry. Tube *E* was then melted off. The apparatus was then reversed again, mercury poured into the seals, and the apparatus evacuated completely with a good mercury pump. Then bromine-water was poured into *D* and carefully brought into the vessel. This was gently heated, and sufficient bromine added until its vapour was just visible in *E*. The vessel was again evacuated, and the gas collected was measured and analysed. The cobalt was determined in the liquid. The following table shows the proportion of cobalt to carbon monoxide found in cobalt tricarbonyl:

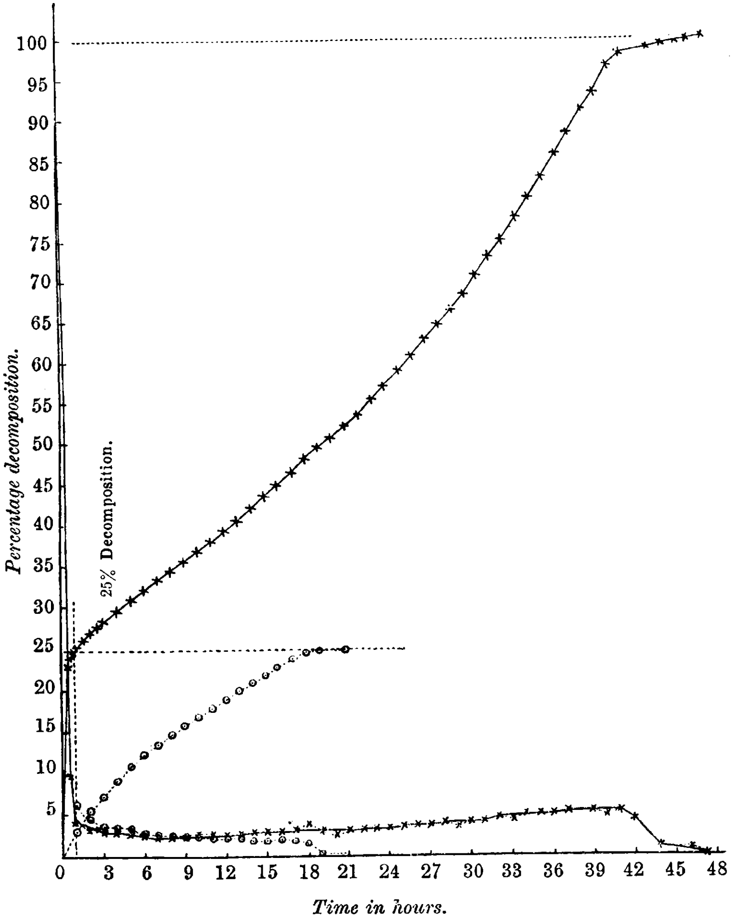
Co (milligrams).	CO (milligrams).	CO/Co in molecular proportion.
48·6	67·3	2·93
75·7	107·3	2·99

It is interesting to notice the further decomposition of the tetracarbonyl. 0·1600 Gram was decomposed at 100°, and the gas evolved was read off at first every fifteen minutes, then every hour. Almost at once a quarter of the carbon monoxide was liberated, then the reaction suddenly slowed down, and continued fairly evenly for twelve hours, when the reaction slowly accelerated again, until between the thirty-sixth and the forty-first hour (the maximum speed) of the reaction was about twice as quick as at the sixth to the ninth hour (the minimum). After the forty-second hour the reaction diminished very suddenly, and was practically completed at the forty-seventh hour, when 99·6 per cent. of the theoretical amount of gas had been given off (see Fig. 3). At 80° and 90° the decomposition was very similar, but proceeded much more slowly. An explanation of this strange behaviour has not yet been found, but from very numerous experiments the following rules can be deducted.

Influence of the Decomposing Vessels.—The larger the volume, the slower is the decomposition. In small vessels the decomposition proceeds comparatively quickly, and no increase of speed could be detected. In comparatively large vessels the decomposition is very slow, and only a slight increase towards the end could be noticed.

Influence of Pressure.—A pressure of 2 atmospheres did not influence the decomposition. In a vacuum the decomposition takes place much more quickly; no increase towards the end could be detected. No re-combination of the products takes place between 15° and 60° whether the decomposition of the carbonyl was complete or whether 25 or 50 per cent. of the theoretical amount of carbon monoxide had been given off. We have not yet been able to establish any relation between the tricarbonyl and hexahydroxybenzene or any other organic compound; neither were we able

FIG. 3.



—✳—✳—✳— (Upper): Decomposition of cobalt carbonyl at 100°.
---⊙---⊙---⊙--- ,, : ,, ,, ,, 60°.
—✳—✳—✳— (Lower): Hourly rate of the decomposition (multiplied by 2) at 100°.
---⊙---⊙---⊙--- ,, : ,, ,, ,, ,, ,, 60°.

to estimate the molecular weight of the tricarbonyl, as the solubility in the usual solvents is too small.

Nickel Carbonyl.

After having carried out the above experiments with cobalt, nickel tetracarbonyl was investigated in the hope of obtaining a compound similar to cobalt tricarbonyl, but so far we have not succeeded in doing so. We endeavoured to decompose nickel tetracarbonyl in an almost complete vacuum at 0°, also by decomposing it in a small vessel fitted with a reflux condenser at 50°, and by subjecting nickel (prepared by reduction) or nickel tetracarbonyl to the action of carbon monoxide under a pressure of 120 atmospheres. Incidentally it was found that when carbon monoxide containing oxygen and nickel carbonyl in molecular proportions is heated to 200°, a colloidal nickel oxide is formed. This is deposited on the heated glass tube, through which the mixture is slowly passed, and forms a yellowish-green layer on the tube; it separates in small flakes having the physical appearance of dried varnish, and if the layer is sufficiently thin it gives beautiful iridescent colours. It is soluble in acids, even in aqua regia, only with great difficulty on prolonged boiling. When heated in hydrogen it forms a nickel mirror.

Iron Carbonyl.

The liquid ferropentacarbonyl is formed under a pressure of 150—250 atmospheres, and at a temperature of 180—220°, without the aid of light. We have not yet succeeded in decomposing this compound.

Molybdenum Carbonyl.

In the case of molybdenum the great difficulty has been to prepare metallic molybdenum in a sufficiently active form. The reduction of the oxides with hydrogen is quite useless, because the temperature at which the reduction takes place is too high to leave the molybdenum in an active state. It is necessary first to prepare an oxychloride by heating a strong solution of molybdenum in nitric acid repeatedly with hydrochloric acid. The oxychloride is then reduced by hydrogen at a low temperature. The molybdenum prepared in this way is not very active; it is just pyrophoric if gently warmed. It was subjected to the action of carbon monoxide at a minimum pressure of 150 atmospheres and at a temperature of about 200°. Under a pressure of about

200—250 atmospheres, a very small quantity of crystals was slowly formed in the cooled glass tube.

Molybdenum carbonyl forms highly refractive, white crystals; the specific gravity measured by the suspension method is 1·96, and it is soluble in ether or benzene. The crystals evaporate before melting, and can easily be sublimed in an atmosphere of hydrogen or carbon monoxide at a temperature of 30° or 40°. The vapours begin to decompose at 150°. The chemical properties resemble those of the other carbonyls. It is scarcely attacked by non-oxidising agents, but quickly by oxidising agents, especially by bromine; carbon monoxide is eliminated, and molybdic acid is left in suspension. Analysis of the crystals gave the following result:

Found, CO = 0·0432 gram. Mo = 0·0279 gram.

This corresponds very nearly with a molecular proportion of CO : Mo = 6 : 1. The formula is therefore $Mo(CO)_6$.

Ruthenium Carbonyl.

If ruthenium black is subjected to the action of carbon monoxide, a very small quantity of a yellow-orange deposit is formed in the cooled glass tube, and a comparatively strong mirror is formed in the heated glass tube. The reaction does not start below a pressure of about 350—450 atmospheres, and a temperature of 300°. The deposit is insoluble in hydrochloric acid, but soluble in nitric acid or bromine, gas being evolved. It contains ruthenium, and forms a ruthenium mirror when heated.

The mirror obtained in the heated glass tube is soluble to a slight extent in hydrochloric acid (solution contains iron). The insoluble part is not dissolved by aqua regia, and consists of ruthenium. Although the quantity hitherto obtained is too small for analysis, we can conclude from the formation of a ruthenium mirror that a ruthenium carbonyl has been produced.

Other Metals.

We have also investigated the action of carbon monoxide on other metals, such as manganese and chromium, which, however, we had great difficulty in obtaining in a suitable pyrophoric form. Reduction of the oxides with hydrogen does not occur even under a pressure of 300 atmospheres and at the temperatures we were able to employ. We obtained these metals in a highly pyrophoric state, however, by Feree's method, which consists in distilling their amalgams in a high vacuum; we also succeeded in preparing them quite free from mercury. Even under pressures up to 500 atmospheres and at temperatures up to 450°, however, we did not observe the least deposit in the cool tube or any mirror in the heated glass tube.

In the case also of tungsten (prepared by reducing the oxides or chlorides with hydrogen or by reducing the oxides with zinc or sodium), no indication of the formation of a carbonyl occurred, although the metal obtained by reducing the oxide with sodium was very much more active than any other form; it was, however, not pyrophoric.

Palladium and rhodium, prepared in the form of black by different methods, also gave no result.

The investigation is being continued.