Facsimile of
L. Mond, C. Langer, and F. Quincke, Action of Carbon Monoxide on Nickel
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values cannot be considered as nearer the truth than about 10′. The limits of the actual observations average about 20′ on each side of the mean values given. But the results are quite conclusive as to the identity of the so-called "isoxylepidenic acid" with ordinary oxylepidenic acid. The disposition of the faces was in all cases similar, *c* being invariably the best developed face, and the optical properties of the two preparations were identical. In the case of the preparation marked oxylepidenic acid, the crystals rarely showed the faces *n* and *t*, but this, which often happens with different preparations of the same substance, was the only point of difference observed.

L.—*Action of Carbon Monoxide on Nickel.*

By Ludwig Mond, Dr. Carl Langer, and Dr. Friedrich Quincke.

When carbon monoxide is passed over finely-divided metallic nickel at a temperature between 350° and 450°, carbon dioxide is formed, and a black, amorphous powder is obtained consisting of nickel and carbon. The composition of this powder varies very widely with the temperature employed, and still more according to the time the operation has been carried on. A small quantity of nickel can decompose a very large amount of carbon monoxide. At the commencement, a fast current of carbon monoxide is completely changed into carbon dioxide by a comparatively small quantity of nickel. By-and-by, the change becomes less complete, but the gas may be passed for several weeks before carbon dioxide ceases to be formed.

We have in this way obtained a product containing as much as 85 per cent. carbon and 15 per cent. nickel. By treating this product with acids, a certain portion of the nickel goes into solution; but we have not been able to extract the nickel completely, the minimum quantity remaining after treatment with concentrated sulphuric acid being 5·59 per cent.; by treatment with dilute hydrochloric acid, 9·30 per cent.*

In order to determine the nickel in this substance, we have heated it with concentrated sulphuric acid to about 200°, and then added nitrate of potash in small portions to oxidise the carbon. This was the only way by which we could obtain a perfectly clear solution, and

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* Gautier and Hallopeau (*Compt. rend.*, **108**, 1889, **1111**) obtained a similar product containing 20·05 per cent. of nickel and 79·95 per cent. carbon, by acting with bisulphide of carbon on metallic nickel.

from this the nickel was precipitated in the usual way. The combustion of the substance with copper oxide or lead chromate in a current of oxygen did not give satisfactory results.

The carbon contained in this substance is very readily attacked by steam; at the comparatively low temperature of 350°, hydrogen and carbon dioxide are obtained without a trace of carbon monoxide.

When we allowed this substance to cool while a current of carbon monoxide was being passed over it, we noticed that the flame of a Bunsen burner into which the escaping gas was introduced became highly luminous, and when we heated the tube through which the gas passed, we obtained a metallic mirror which proved to be nickel mixed with a small quantity of carbon.

After further investigating this subject, we found that the gas contains a compound of nickel and carbon monoxide, which we propose to call nickel-carbon-oxide.

When a finely-divided nickel, such as is obtained by reducing nickel oxide by hydrogen at about 400° is allowed to cool in a slow current of carbon monoxide, this gas is very readily absorbed as soon as the temperature has descended to about 100°, and if the current of carbon monoxide is continued, or if this gas is replaced by a current of an inert gas (such as carbon dioxide, nitrogen, hydrogen, or even air) a mixture of gases is obtained which contains upwards of 30 per cent. of nickel-carbon-oxide. After a time (with a moderate current of gas, about an hour), the quantity of this compound given off becomes less and gradually diminishes till it practically ceases altogether. The property of the nickel to form this compound is restored by heating it again to about 400°, and cooling it down; and, for a time, it yields the compound more abundantly after repeated use. When these mixtures of gases are heated above 150°, their volume increases and nickel separates, which, according to the temperature, is more or less contaminated with carbon resulting from the action of the nickel upon the carbon monoxide generated.

After ascertaining that at a temperature of 180° nickel quite free from carbon is deposited, we have analysed these mixtures of gases, after absorbing the excess of carbon monoxide by cuprous chloride, by passing them repeatedly through a capillary tube inserted in aniline vapour until the volume became constant, weighing the nickel deposited in the tube, and ascertaining the volume of carbon monoxide formed by this decomposition. This volume was found to be in the proportion of 4 to 3 to the volume by which the original gas had been increased, thus proving that one volume of our compound gives 4 volumes of carbon monoxide. We give the result of several analyses, which lead to the formula $Ni(CO)_4$.

Gas volume.	After decomposition.	Expansion.	CO formed.	N.	Deposited Ni.
1. 28·3 c.c.........	59·8	31·5	41·8	18·0	0·0260 gram
2. 48·5 c.c.........	96·0	47·5	63·3	32·7	0·0438 „

For 100 c.c. of the nickel-carbon-oxide vapour (gas volume—nitrogen) this comes to—

(1.) 405·9 c.c. CO and 0·2527 gram Ni.
(2.) 400·5 c.c. CO and 0·2772 gram Ni.

The formula $Ni(CO)_4$ requires 400 c.c. CO and 0·2615 gram Ni.

The vapour of nickel-carbon-oxide when mixed with other gases is not acted upon by alkalis or acids; but it reduces a solution of copper chloride in ammonia, which becomes first decolorised and subsequently copper is precipitated from it. It also throws down silver from ammoniacal solutions of silver chloride. Chlorine decomposes it with formation of nickel chloride and carbon oxychloride. Bromine has a similar action. An electric spark decomposes it slowly into nickel and carbon monoxide. The presence of this vapour in other gases is very readily shown by the luminosity of the Bunsen flame into which it is introduced; very small quantities still show red luminous streaks.

If a mixture of gases containing the vapour of nickel-carbon-oxide is passed through a tube placed in a refrigerating mixture of salt and ice, the nickel-carbon-oxide is condensed to a colourless, mobile liquid of very high refractive power.

To obtain some quantity of this liquid, a combustion tube is filled with nickel oxide, the oxide reduced at about 400° by hydrogen, cooled down to about 30°, and pure and dry carbon monoxide is then passed through this tube without further heating it; the gas issuing from the tube is passed through a Y-tube surrounded by a freezing mixture of salt and ice. The lower end of this tube projects through the vessel containing the freezing mixture, and is connected to a small flask in which the condensed liquid accumulates. The gas, which on leaving the Y-tube still contains about 5 vols. per cent. of nickel-carbon-oxide, is collected, dried, and passed repeatedly over the nickel. When no more liquid condenses, the tube containing the nickel is heated up to about 400° in a slow current of pure hydrogen, cooled down again, and the operation recommenced. In this way we obtained from 10 to 15 grams of liquid in each operation.

The boiling point of this liquid, we found to be 43° at 751 mm.

pressure. Its sp. gr. is 1·3185 at 17°; at − 25° it solidifies, forming needle-shaped crystals.

The liquid is soluble in alcohol, but more readily soluble in benzene and chloroform. It is not acted upon by dilute acids and alkalis or by concentrated hydrochloric acid. Concentrated nitric acid and aqua regia oxidise it readily.

We have determined the nickel in this liquid by vaporising it in a current of hydrogen, and passing the vapour repeatedly through a U-tube heated in aniline vapour, and weighing the nickel deposited; and the carbon, by passing the vapour in a current of air over copper oxide, and weighing the carbon dioxide formed. We have thus obtained the following results:—

I. 0·0917 gram substance gave 0·0306 gram nickel = 33·35 per cent.
II. 0·0950 gram substance gave 0·0316 gram nickel = 33·37 per cent.
III. 0·2410 gram substance gave 0·2556 gram CO_2 = 66·60 per cent. CO.
IV. 0·2672 gram substance gave 0·2736 gram CO_2 = 65·99 per cent. CO.

The formula $Ni(CO)_4$ requires 34·34 per cent. nickel and 65·66 per cent. CO. The difference between the calculated amounts and the amounts found is probably due to carbon monoxide dissolved in the liquid.

The vapour density of the liquid determined by Victor Meyer's method at 50° has given the following figures:—

0·1052 gram substance displaced 14·4 c.c. air measured moist at 16° and 768 mm. pressure.

From this it follows that the density is 6·01. The formula $Ni(CO)_4$ requires 5·9. At a temperature of 60°, the vapour of the liquid explodes violently. This is the first determination of the vapour density of a compound of nickel, and shows the atomic volume of nickel to be near 58.

We have at present no suggestion to offer as to the constitution of this remarkable compound, but it is our intention to fully investigate this problem, and more particularly to study its action upon organic bodies.

Numerous experiments made to obtain similar compounds of carbon monoxide with other metals, notably with cobalt, iron, copper, and platinum, have only led to negative results, although they were carried out at temperatures from 15° to 750°. In experimenting with specially purified metallic cobalt, we obtained in the beginning a small coloration of the Bunsen flame, which completely disappeared after some time. In using commercial cobalt, we obtained a gas which yielded metallic mirrors. These, however, consisted of pure nickel, and did not show any of the reactions of cobalt. It seems thus possible to purify cobalt entirely from nickel by treating it with carbon monoxide. The metallic mirrors which we obtained from the nickel-carbon-oxide gave remarkably pure nickel reactions, and did not show a trace of any of the reactions of cobalt. The metal obtained from these mirrors by solution in acid, precipitation with ammonia, and reduction with hydrogen is a grey, metallic powder, the specific gravity of which we found to be 8·2834 at 15·4° and 8·2928 at 15·1°. The very finely divided metal is easily soluble in acids.

We had obtained a small quantity of this pure metal from a considerable quantity of nickel which had been under treatment. It appeared to us worth while to approximately determine the atomic weight of this pure metal, as this might throw some light upon the elementary nature of nickel and its real atomic weight, which have recently been called in question by Krüss and Schmidt, who expressed the opinion that the latter was considerably below the accepted figure. If this opinion were correct, the atomic weight of the metal obtained by us would presumably differ considerably from the figure obtained for nickel by previous investigators. For this purpose the mirrors obtained were dissolved in aqua regia, evaporated, redissolved in water, and ammonia added until the liquid was coloured blue, filtered, evaporated again, and heated in an open platinum crucible, with access of air, until the weight remained constant. The nickel oxide so obtained was then reduced by hydrogen (made by electrolysis), at a temperature of 500°, until the weight remained constant. In this way the following results were found :—

	Reduced.		Atomic weight. calculated for O = 16.
(1.)	0·2414 gram NiO	0·1896 gram Ni	58·58
(2.)	0·3186 „	0·2503 „	58·64
(3.)	0·3391 „	0·2663 „	58·52

These figures agree sufficiently well with the atomic weight as determined by Russell (= 58·74) to justify the conclusion that the old nickel as we have known it for a great number of years is a simple substance, the atomic weight of which lies very near to the figure hitherto accepted.