

LIV.—*Note on a Volatile Compound of Iron with Carbonic Oxide.*

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IN a paper on the action of carbonic oxide on nickel communicated to the Society (Trans., 1890, **57**, 749) by us in conjunction with Dr. Carl Langer, and which dealt with the preparation and properties of nickel-carbon-oxide, it was stated (p. 752) that all experiments to obtain a similar compound with other metals had been unsuccessful. Considering it very improbable that nickel should be the only metal forming such a compound, we have continued these experiments, more particularly with iron, under very varied condi-

tions, and have succeeded in volatilising notable, although very small, quantities of iron in a current of carbonic oxide.

If very finely-divided iron, obtained by reducing iron oxalate in a current of hydrogen at the lowest possible temperature, exceeding but little 400° , is allowed to cool in hydrogen gas to 80° , and then treated with carbonic oxide, the issuing gas imparts a yellow colour to the flame of a Bunsen burner into which it is introduced, which continues even at ordinary temperature for several hours; and by passing it through a heated glass tube, a metallic mirror is formed at between 200° and 350° , whilst at higher temperatures, black flakes are produced.

On dissolving these mirrors, the solutions gave all the known reactions of iron in remarkably brilliant colours. The oxide obtained by dissolving the mirror in nitric acid, precipitating with ammonia, and heating to constant weight, was reduced by hydrogen. We obtained from 0.3119 gram of oxide 0.2199 gram Fe = 70.48 per cent., and from 0.4342 gram of oxide 0.3037 gram Fe = 69.94 per cent. Fe = 56, O = 16 require 70.00 per cent. There can thus be no doubt that these mirrors consist of iron. The black flakes obtained at higher temperature consist of iron and carbon. By the combustion of the substance and absorption by caustic potash of the carbonic acid formed, we found 79.30 per cent. of carbon.

However, even under the most favourable circumstances, the quantity of iron obtained in this way is very small. Treating 12 grams of finely-divided iron with carbonic oxide during six weeks, we volatilised only about 2 grams of iron. As the action of the carbonic oxide became less energetic after a time, we had to interrupt the operation and heat the iron at 400° in a current of hydrogen for about 20 minutes every five or six hours. By passing $2\frac{1}{2}$ litres of carbonic oxide per hour over the iron, the issuing gas contained at its best not more than 0.01 gram of iron, which corresponds (if we assume the volatile iron compound to have the same composition as nickel-carbon-oxide) to less than 2 c.c. of the compound in a litre of gas.

This great dilution makes the study of the properties and composition of the compound very difficult.

In passing the gas containing it through sulphuric acid, the compound is completely absorbed, but the solution decomposes very rapidly.

In passing the gases through benzene or heavy mineral or tar oils, the compound is partially absorbed, but all the substances we have tried only take up a small quantity of it. The solutions obtained are of a tawny colour, and decompose on exposure to the air, with separation of iron hydroxide.

The solutions in mineral oils boiling between 250° and 300° seemed to us the most suitable for studying the composition of the compound; but we found it impossible to exhaust it from these solutions by means of the vacuum pump.

On raising the temperature of the solution to 100° the solution remained clear, and under a pressure of 500 mm. mercury, we obtained only a small quantity of a mixture of air and carbonic oxide (from 30 c.c. of oil about 5 c.c. of gas).

On raising the temperature to about 180°, the solution turned black, from separated metallic iron, which was found to be free from carbon, and carbonic oxide was slowly evolved; this sometimes contained a very small quantity of carbonic acid, but was always quite free from hydrogen.

We have determined the quantity of iron and carbonic oxide obtained, by heating about 30 c.c. of heavy mineral oil, through which the gas containing our compound had been passed from 8 to 16 hours, in a glass vessel very nearly filled with the oil, and connected by a capillary tube to a Hempel burette filled with mercury.

The tube was heated to 100° under a vacuum of 500 mm. mercury until the volume in the burette remained constant; the tube was cooled down to measure the exact volume of this gas, and was then heated up to 180° until no more gas was evolved, which took from 1 to 2½ hours. The increase in the volume of the gas by the latter operation gave us the carbonic oxide in the compound.

The iron contained in the oil was, after dilution with ether if necessary, collected on a filter and converted into oxide. The filtrate was distilled off, and the small residuum treated with hydrochloric acid and precipitated with ammonia, and the resulting small quantity of oxide of iron added to the first. In this way we obtained the following results:—

No.	Solvent.	Found.		Corresponding to		Calculated.		
		Increase of volume at 0° and 760 mm.	Fe ₂ O ₃ .	CO.	Fe.	1 atom Fe to 4 atoms CO.	Proportion of atoms CO to 1 Fe.	Quantity absorbed of Fe(CO) ₄ = ¼CO.
		c.c.	gram.	gram.	gram.	gram.		
1...	Paraffin oil ..	31·32	0·0270	0·03917	0·01890	0·01958	4·144	7·83
2...	Petroleum oil	34·29	0·0304	0·04288	0·02128	0·02144	4·030	8·57
3...	„	20·2	0·0174	0·02527	0·01218	0·01263	4·150	5·05
4...	Kerosine	38·18	0·0320	0·04775	0·02240	0·02387	4·264	9·54
5 ..	„	50·45	0·0446	0·06310	0·03122	0·03155	4·042	12·61

These figures, although only approximate on account of the very small quantities of substance and the imperfect method we had to use for their determination, make it very probable that the volatile iron compound is iron-tetra-carbonyl, $\text{Fe}(\text{CO})_4$, analogous to nickel-tetra-carbonyl, $\text{Ni}(\text{CO})_4$.
