

XIX.—*Behaviour of the more Stable Oxides at High Temperatures.*
(Part I.) *Cupric Oxide.*

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FROM a number of statements which occur in works on metallurgy, and observations made on changes which take place when cupric oxide is exposed to high temperatures, it is quite evident that under such circumstances there is a loss of oxygen. In most cases the observer has contented himself with stating that the product obtained is cuprous oxide, without giving the grounds on which this conclusion is based. On the other hand, however, there exist records of experiments in which the conditions of working and the products obtained are carefully described, and it will be of interest in regard to the results arrived at by us to give a brief *résumé* of the investigations which have been made on the lower oxides of copper. The earliest of these appeared in 1845 (*Compt. rend.*, **18**, 658), when Favre and Maumené, by heating cupric oxide at the temperature of melting copper, obtained a dark-coloured substance having the composition Cu_5O_3 . Although oxygen was given off freely at this temperature, it was taken up again at a cherry-red heat.

Vogel and Reischauer (*Jahresb. Chem.*, 1859, 216) obtained cuprous oxide by heating cupric oxide, and Marchand (*J. pr. Chem.*, **20**, 505) found that on exposing cupric oxide in a muffle for half an hour at a white heat, and then for eight hours at a dull-red heat, the product remaining had the composition Cu_2O .

Without mentioning the many well-known reactions in which cuprous oxide is formed, it may be remarked that Gladstone and Tribe (*Chem. News*, **25**, 193) observed it as a yellow coating when a copper-silver couple was placed in a solution of nitrate of copper. The hydrated oxides prepared by Siewert (*Zeitschrift für Chemie*, 1866, 363), $\text{Cu}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}_4\text{O}_3 \cdot 5\text{H}_2\text{O}$, and the tetrantoxide, Cu_4O (hydrated), of Rose (*Ann. Chem. Phys.*, **120**, 1) must also be mentioned.

With the exception of Rose's oxide, all these may be classified on the assumption that they are derivatives of cuprous and cupric oxides:—

Rose's oxide	Cu_4O
Cuprous oxide	Cu_2O (and cuprite).
Favre and Maumné's oxide	$2\text{Cu}_2\text{O}, \text{CuO}$.
Siewert's oxide (a)	$\text{Cu}_3\text{O}_2, \text{CuO}, 2\text{H}_2\text{O}$.
" " (b)	$\text{Cu}_4\text{O}_3, 2\text{CuO}, 5\text{H}_2\text{O}$.

That cuprous oxide is obtained when cupric oxide is exposed in an oxidising atmosphere at a moderate temperature seems pretty conclusively shown.

Our object at the outset of this investigation was to examine whether cuprous oxide is the ultimate product when cupric oxide is exposed to high temperatures, or whether by using higher temperatures a further loss of oxygen took place.

Method of Experiment.

Finely-powdered cupric oxide was exposed to a white heat in a Fletcher injector-furnace, care being taken to preserve an oxidising atmosphere during the course of the experiment. At the temperature used, fire-clay crucibles were attacked by the copper oxide with the formation of a fusible slag, so that in most of the experiments recorded in this paper recourse was had to lime crucibles. As the temperature rose the oxide fused, and then bubbles of gas were seen to come off freely, the heating being continued—at least so long as there appeared to be any gas given off.

On cooling, a yellowish-red mass was obtained hard enough to scratch glass quite easily, and having the sp. gr. 3·81. A thin film of black oxide with which it was coated (and which evidently formed during the process of cooling down) was removed, though, indeed, it was so thin that it could hardly have affected the analytical determinations.

Analysis of Product.

The finely-powdered oxide was analysed by reduction in a stream of dry hydrogen, the water which was formed being absorbed in a calcium chloride tube in the usual manner, whilst the weight of copper remaining in the boat afforded a check on the results.

Several experiments were made, the time during which the oxide was exposed varying from one to three hours. In all cases the product obtained had the same properties and composition, the percentage of oxygen being always found to fall between 7 and 8 per cent.

A larger quantity was now prepared, the central portion of which was taken for analysis so as to be sure that no particles of lime had found their way into it. The results of the analysis were as follow :—

Substance taken.....	0·615	gram.
Water obtained	0·0535	„
Copper „	0·568	„
Copper (by difference)	0·5655	„

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The percentage composition calculated from these numbers agrees well with that required for Cu_3O :—

	Found.	Calculated.
Copper.....	92·36	92·23
Oxygen.....	7·73	7·77

For the sake of comparison, it may be stated that the oxides Cu_2O and Cu_4O contain 11·22 and 5·94 per cent. of oxygen respectively.

Although every care was taken to preserve an oxidising atmosphere in the furnace, further proof was deemed desirable that the loss of oxygen was not due to reducing action of the flame. A piece of hard lime was therefore hollowed out, and in this the oxide was exposed to the oxy-hydrogen or rather oxy-coal gas flame, in such a way that only the extreme point of the oxidising flame was allowed to play upon it. Fusion took place as before, and gas was observed to be given off; when the evolution of gas had ceased the mass was allowed to cool. The product in all respects resembled that obtained in the Fletcher furnace, and where it came in contact with the lime there was formed a bright vermilion coating which consisted of lime and a lower oxide of copper, but which was not further examined. The results of two determinations were :—

	I.	II.
Substance taken	0·564	0·494
Water obtained	0·045	0·042
Copper „	0·524	0·457
Copper (by difference) ...	0·524	0·456

We have thus :—

	I.	II.	Calculated.
Copper.....	92·90	92·51	92·23
Oxygen.....	7·09	7·55	7·77

The results of the analysis show that the product obtained at the higher temperature is substantially the same as that obtained at the lower, and that it therefore maintains a constant composition within a fairly wide range of temperature, the limits of which we consider are approximately 1500° and 2000° C.; at any rate platinum readily fuses at the higher temperature used. From this it appears that as the oxides of smaller stability give up oxygen at moderate temperatures, so the more stable oxides, such as oxide of copper, are transformed into lower oxides at higher temperatures without the intervention of any reducing agent. Furthermore, as the evidence of several experimenters seems conclusive that cuprous oxide is obtained when a dull-red heat is used, there is—especially if we include Rose's oxide—an indication that the points of stability occur at definite

stages in the process of transformation into the lower oxide, since we have the series Cu_4O , Cu_3O , Cu_2O , CuO . And although our object in this research is rather to accentuate the behaviour of oxides when exposed to high temperatures, it does seem as though sufficient evidence existed for the assumption that Cu_3O may be regarded as a definite oxide of copper, especially when its properties as given below are taken into consideration.

Action of Reagents on Cu_3O .

Even when reduced to the finest state of division in an agate mortar, the oxide is entirely unacted on by concentrated (or dilute) mineral acids; even aqua regia and boiling concentrated sulphuric acid are without action. Hydrofluoric acid, however, slowly attacks it with the formation of a blue, crystalline fluoride of copper which has not been further examined. The only method by which we were able to bring the oxide into solution for the purpose of confirming the analysis by an entirely different process was to fuse it with caustic potash, in which it dissolved with a blue colour, and from which it separated again on the addition of water in flocculent, brown particles. This, dissolved in sulphuric acid and titrated with potassium permanganate, was found to contain 9.8 per cent. of oxygen, a result falling about midway between Cu_3O and Cu_2O ; it was, however, to be expected that some oxidation would take place in the process of fusion and extraction with water; in spite of this, however, the product contained less oxygen than Cu_2O .

It would be interesting to analyse a number of samples of native cuprite in order to see if they yielded any indication of exposure to temperatures such as were used in these experiments. We are continuing the work and proceeding with the examination of other oxides, and have indeed already obtained evidence that litharge, sesquioxide of bismuth, and vanadic acid lose oxygen in the same way as cupric oxide.
