

XLIII.—*The Preparation of Cadmium Suboxide.*

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VARIOUS suboxides of cadmium have long ago been described (Tanatar, *Zeitsch. anorg. Chem.*, 1901, **27**, 433; Morse and Jones, *Amer. Chem. J.*, 1890, **12**, 488, etc.), although other investigators have thrown doubt on the existence of these suboxides. The following experiments describe the efforts made to prepare a suboxide of cadmium in as pure a state as has been the case with lead suboxide.

*Decomposition of Cadmium Oxalate.*

The first method attempted was that described by Tanatar (*loc. cit.*), namely, the decomposition of the oxalate in a stream of carbon dioxide. A sample of cadmium oxalate ( $\text{Cd}=56.02$  per cent.) was heated at  $300^{\circ}$  in a rapid stream of carbon dioxide freed from traces of oxygen by passage through heated copper. At the end of forty-eight hours the evolution of gas ceased, and examination revealed a small quantity of a green material, unmistakably containing globules of cadmium, whilst the leading tubes were lined with a deposit of the volatilised metal. This experiment, many times repeated, always gave the same result.

Precisely similar results were obtained when the carbon dioxide was not employed, the evolved gases being removed by means of a Sprengel pump. Even when the total pressure of these gases did not exceed 1 mm., the same green, heterogeneous substance was produced. Analysis of this material always gave values closely approximating to  $\text{Cd}=96.5$  per cent. (Tanatar's  $\text{Cd}_4\text{O}$  contains  $\text{Cd}=96.56$  per cent.).

Tanatar and Levin (*loc. cit.*) also describe how the oxide,  $\text{Cd}_2\text{O}$ , was obtained by the decomposition of a basic oxalate under similar conditions. A repetition of their experiment always gave a heterogeneous grey mass containing free cadmium.

An attempt was then made to remove by distillation the excess of metal present in the decomposition product of the oxalate. The mixture was heated to  $350^\circ$  without undergoing any change in appearance. The pump was then put into requisition, and in ten hours a large deposit of cadmium had volatilised out of the oven, whilst the residue was a homogeneous green mass, in which the microscope was no longer able to detect free metal. The following analytical results were obtained:

Oxalate. Grams.	Green substance. Gram.	$\text{CdSO}_4$ . Gram.	Cd. per cent.
2.0	0.0362	0.0628	93.5
2.5	0.0592	0.1025	93.4
2.0	0.0809	0.1401	93.4

$\text{Cd}_2\text{O}$  requires Cd = 93.36 per cent.

The method therefore appears to give a green oxide, but owing to the strong reducing action of the evolved carbon monoxide and the difficulty of distilling out the free metal, the method is not satisfactory.

#### *Reduction by Hydrogen.*

An attempt was made to prepare the suboxide by reducing the brown oxide with hydrogen (see Glaser, *Zeitsch. anorg. Chem.*, 1903, **36**, 1). At  $240^\circ$ , after twenty hours' reduction, the yellowish-green product appeared to be uniform, but the microscope clearly revealed globules of free metal. Reduction under varying conditions of temperature and pressure always led to this result. The excess of metal was afterwards removed by distillation, and a uniform, yellowish-green product obtained, in which the microscope revealed no sign of free metal. Analysis, however, showed that this substance was pure cadmium oxide ( $\text{CdO}$ ), the colour change being either superficial or due to a different molecular aggregation.

#### *Reduction by Carbon Monoxide.*

It has been shown by Brislee (T., 1908, **93**, 162) that the time-reduction curve of cadmium oxide at  $300^\circ$ , with carbon monoxide as the reducing agent, shows a distinct break at a point which corresponds with the compound  $\text{Cd}_2\text{O}$ . Although it appeared

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difficult to stop the reduction at the precise moment when the whole of the higher oxide had been reduced to the suboxide and none of the latter to the metal, it seemed feasible to carry through the reduction in such a way that the higher oxide was reduced to a mixture of the suboxide and metal, and this metal could then be removed by volatilisation.

An analysis of Brislee's time-reduction curve for  $300^{\circ}$  shows that the break occurs when the reduction has progressed for about twelve hours. An experiment was therefore carried out in which carbon monoxide was circulated for fourteen hours at  $300^{\circ}$  through two bulbs, each containing about 0.6 gram of cadmium oxide. One bulb was then sealed off, and the other heated in a vacuum for eighteen hours. The material in the first bulb was yellowish-green, containing visible globules of cadmium, whilst the second bulb gave a perfectly uniform, yellowish-green substance. Bulb I contained  $\text{Cd}=90.4$  and bulb II  $\text{Cd}=87.5$ , whilst  $\text{CdO}$  requires  $\text{Cd}=87.57$  per cent. This experiment was repeatedly carried out at various temperatures between  $300^{\circ}$  and  $310^{\circ}$ , and in all cases the bulb sealed off before exhaustion contained a considerably higher percentage of cadmium than does  $\text{CdO}$ , approximating often to that of  $\text{Cd}_2\text{O}$ , but a moderately good pocket lens was sufficient in every case to show that the reduction product was heterogeneous and contained cadmium. Similarly, the bulb from which the excess of cadmium had been volatilised at the temperature of the experiment always gave a uniform, yellowish-green product exactly similar to that obtained when hydrogen was the reducing agent, and the composition of this was undoubtedly that of  $\text{CdO}$ . As a means of preparation of cadmium suboxide, this method therefore fails.

*Morse and Jones's Method.*

Morse and Jones (*loc. cit.*) have described how anhydrous cadmium chloride, when fused with cadmium, gives a product having the composition  $\text{Cd}_4\text{Cl}_7$ . This they consider to be possibly a mixture of  $3\text{CdCl}_2 + \text{CdCl}$ . On treatment with water, the product gave cadmous hydroxide, from which yellow cadmous oxide,  $\text{Cd}_2\text{O}$ , was readily obtained by dehydration. The author has repeated this work, and succeeded in reproducing the results described by Morse and Jones, but in spite of close attention to the details given in the original publication, he has never succeeded in converting more than 5 per cent. of the original chloride into suboxide, so that, as a practical method of preparing the suboxide in quantity, the method is not satisfactory.

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In conclusion, it may be stated that the suboxide of cadmium may be obtained in small quantity by the method described by Morse and Jones, as well as by the decomposition of cadmium oxalate. The latter method, however, is only of use when the excess of metal, always formed during the decomposition, is distilled off in a vacuum, but the amount of residual cadmium suboxide is never more than 4 per cent. by weight of the original oxalate.

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