222. *The Non-existence of Cadmous Compounds.*

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The literature contains somewhat conflicting accounts of cadmous compounds and sub-compounds of cadmium. Morse and Jones (*Amer. Chem. J.*, 1890, **12**, 488) prepared the substances Cd_4Cl_7, Cd_4Br_7, and $Cd_{12}I_{23}$, by fusing the anhydrous halide with excess of metallic cadmium in nitrogen. They consider the first of these to be a mixture of 1 mol. of cadmous with 3 mols. of cadmic chloride. Mellor (" Comprehensive Treatise, etc.," IV, p. 548), without offering any evidence, regards these compounds as probably solid solutions of cadmium in the corresponding halide. Aten (*Z. physikal. Chem.*, 1910, **73**, 593) examined the fusion curve of mixtures of cadmium and cadmic chloride and failed to find any evidence of the existence of cadmous chloride or of any sub-chloride; he also noted the presence of free cadmium in the solidified melts.

It is claimed that the above-named halides give cadmous hydroxide when treated with water for prolonged periods, and this substance on dehydration gives a yellow cadmous oxide, Cd_2O. Tanatar (*Z. anorg. Chem.*, 1901, **27**, 433), by heating cadmium oxalate at 300° in carbon dioxide, obtained a green sub-oxide, Cd_4O, whilst Tanatar and Levin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495), by a similar treatment of a basic oxalate, obtained cadmous oxide. Glaser (*Z. anorg. Chem.*, 1903, **36**, 1) claims to have obtained a sub-oxide of unstated composition by the reduction of cadmic oxide with hydrogen at 240°, and Brislee (J., 1908, **93**, 162) finds a break in the time–reduction curve at the composition corresponding with cadmous oxide on heating cadmic oxide with carbon monoxide at 300°. Denham (J., 1919, **115**, 556) finds that cadmous oxide may be obtained in small quantity by the methods of Morse and Jones and of Tanatar (*locc. cit.*), and he shows that the compound, Cd_4O, contains free metal, which on removal by distillation gives an apparently pure cadmous oxide, the yield, however, never exceeding 4%. He also finds that the material obtained by the methods of Glaser and of Brislee contains free cadmium, and removal of the metal by distillation leaves cadmic oxide.

We have examined the above substances with the object of ascertaining whether they are definite compounds or mixtures.

The sub-chloride, Cd_4Cl_7, is shown to be a mixture $Cd + 7CdCl_2$. Von Hevesy and Löwenstein (*Z. anorg. Chem.*, 1930, **187**, 266) confirm Aten's fusion results and show that the solubility of metallic cadmium in molten anhydrous cadmic chloride is 0·18 and 0·195 atom per mol. at 600° and 635° respectively. At the temperature of preparation of the sub-chloride (*ca.* 550°) the solubility extrapolated from von Hevesy's values is 0·158 atom per mol., which practically corresponds with the free cadmium in the 1 : 7 mixture. Morse and Jones (*loc. cit.*) by the action of dilute hydrochloric acid obtained hydrogen corresponding to the sub-chloride, but a 1 : 7 mixture must give the same volume of hydrogen by the same treatment.

The atomic susceptibility of cadmium in the sub-chloride is $-27{\cdot}3 \times 10^{-6}$, the mean value calculated from a series of 30 cadmic compounds investigated by us being $-25{\cdot}1 \times 10^{-6}$, which indicates that cadmium contained in this substance is also bivalent.

Cadmous hydroxide, prepared by Morse and Jones's method, contains more cadmium than is required by the formula CdOH and the composition varies in different preparations. This fact is probably to be attributed to the solubility of cadmic hydroxide in water. The material obviously contained free metal, for when we attempted to hasten its formation from the sub-chloride by centrifuging with water, the product settled to a crystalline metallic layer and a white suspension of cadmic hydroxide. Washing with very dilute hydrochloric acid left a residue of metallic cadmium which corresponds in amount with that required by an equimolecular mixture of cadmium and cadmic hydroxide. In this case also, grinding with mercury removed free cadmium from the material.

The sub-oxide, Cd_4O, prepared by Tanatar's method, was not uniform and had not the composition allotted to it; also it contained free metal, as did the oxide Cd_2O. The temperature of dehydration of the latter was the same as that of cadmic hydroxide.

The evidence submitted indicates that the sub-chloride of Morse and Jones is a mixture of cadmium and cadmic chloride in the molecular ratio 1 : 7, and that the so-called cadmous oxide and hydroxide are equimolecular mixtures of the metal and the corresponding cadmic compounds.

EXPERIMENTAL.

Cadmium sub-chloride was prepared by melting 12 g. of anhydrous cadmic chloride with 6 g. of cadmium and heating the molten mass, with shaking, for 5 hours at about 550° in nitrogen. Excess cadmium was allowed to settle, and on cooling, the sub-chloride was obtained as a grey mica-like crystalline mass, which appeared homogeneous to the naked eye but under the microscope showed crystalline metallic particles (Found : Cl, 35·58. Calc. for Cd_4Cl_7: Cl, 35·65%). When ground in a mortar, the material left metallic streaks. It dissolved very slowly in dilute hydrochloric and sulphuric acids, but with nitric acid there was rapid evolution of oxides of nitrogen. When the dry substance was rubbed with distilled mercury in a mortar, the metallic globules removed, and the mercury distilled, cadmic oxide remained. A weighed quantity of the sub-chloride was washed with cold absolute alcohol on a sintered-glass crucible until the filtrate was free from chloride, and the grey residue of metallic cadmium was weighed (Found : Cd, 8·14. Calc. for $7CdCl_2 + Cd$: Cd, 8·05%).

The mass susceptibility of the sub-chloride was determined by Gouy's method, as modified by Sugden (J., **1932**, 161) and then by Trew and Watkins (*Trans. Faraday Soc.*, 1933, **29**, 1310). The mean of ten determinations gave $-0{\cdot}357 \times 10^{-6}$ (limits $-0{\cdot}355$ and $-0{\cdot}359 \times 10^{-6}$). This value lies at the point corresponding to a mixture $Cd + 7CdCl_2$ on the susceptibility–composition graph for mixtures of the two substances, constructed from the newly determined mass susceptibilities: Cd $-0{\cdot}167 \times 10^{-6}$ (limits $-0{\cdot}166$ and $-0{\cdot}167 \times 10^{-6}$), $CdCl_2$ $-0{\cdot}375 \times 10^{-6}$ (limits $-0{\cdot}372$ and $-0{\cdot}376 \times 10^{-6}$).

Cadmous hydroxide was prepared by the exhaustive washing of freshly prepared powdered sub-chloride with water until the filtrate was free from chloride (Morse and Jones), and the residue dried over phosphoric oxide. The product was a grey heterogeneous powder which gave metallic streaks when rubbed in a mortar. Total cadmium was determined by conversion into the sulphate, and electrolysis of the sulphate solution by a current of 1·4—1·6 amps. and 4·5—4·8 volts with a rotating platinum cathode (Fischer, "Elektroanalytische Schnellmethoden," 1908) (Found : Cd, 88·08, 89·20. Calc. for CdOH : Cd, 86·8%). The free cadmium was determined by washing a weighed quantity on a sintered-glass crucible with 0·3*N*-hydrochloric acid until the filtrate was free from chloride [Found : free Cd, 44·4, 42·1. Calc. for $Cd + Cd(OH)_2$: Cd, 43·42%].

Attempts to determine the mass susceptibility failed because, on packing the tube, free cadmium adhered to the walls and consequently the material was not evenly distributed over the magnetic field; further, in the process of packing, the tube became strongly electrified.

Cadmous oxide was prepared by dehydrating cadmous hydroxide in nitrogen; the loss of water began at 260° and was complete at 280°. Rose (*Pogg. Ann.*, 1830, **20**, 152) gives 300° as the dehydration temperature of cadmic hydroxide. A repetition of this determination under the conditions stated above gave figures identical with those for cadmous hydroxide. Different preparations varied in colour from olive-green to yellow; the composition was variable, and the cadmium content deficient (Found : Cd, 90·89, 90·31. Cd_2O requires 93·35%). Grinding with mercury removed free cadmium, and an estimation made as in the case of the hydroxide gave free cadmium, 46·04 (Calc. for $Cd + Cd_2O$: Cd, 46·68%). Similar conditions to those with the hydroxide prevented a determination of the mass susceptibility.

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