IV.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. VII. *On Bismuth and Bismuth Compounds.*

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PART I.—*On the Oxides and Hydrates of Bismuth.*

A SERIES of papers has been published in this Journal by one of us, on various compounds of bismuth. It is proposed now to study in more detail the chemical habitudes of groups of these compounds.

§. *Preparation of Oxides and Hydrated Oxides of Bismuth.*

A large amount of work on the oxides of bismuth has been published; methods for preparing these salts are not yet, however, clearly established.

Observers are all agreed as to the preparation of bismuthous oxide: this forms the starting point in the preparation of the other oxides.

1. Our experiments have convinced us that by boiling previously prepared bismuthous oxide with potash and alkaline hypochlorite, it is very difficult, if not impossible, to obtain a pure oxide higher than bismuthous oxide (see Arppe, *Pogg. Ann.*, **64**, 237; and Schrader, *Annalen*, **121**, 204). A brown substance is certainly produced, but analyses show that the composition is not homogeneous: in one instance we found 91·5, in another 94·5 per cent. of bismuth. This brown substance does not lose weight until heated to 250°; it does not, therefore, contain bismuthic oxide. It dissolves slowly in strong nitric acid with evolution of oxygen; it therefore contains an oxide higher than bismuthous oxide.

We obtained from Messrs. Hopkin and Williams a black-brown powder labelled "peroxide of bismuth," which, as Messrs. Hopkin and Williams kindly informed us, was prepared "by boiling oxide of bismuth with hypochlorite of soda containing a considerable excess of caustic soda." This substance contained 85·67 per cent. of bismuth (mean of 85·5 and 85·85), 0·76 per cent. moisture, and 1·5 per cent. sodium. The percentage of bismuth calculated on the dry salt free from soda amounted to 88·10 (Bi_2O_4 requires 86·78, and Bi_2O_3 89·75 per cent.). This salt when boiled for some hours with very dilute nitric acid became brown, and was then free from soda. Dried at

130°, it now contained 82·46 per cent. bismuth (mean of 82·57 and 82·35), and 0·30 per cent. moisture. The original black "peroxide" began to change colour and lose weight at 250—260°. It dissolved in hydrochloric acid with evolution of chlorine, and in hot nitric acid with evolution of oxygen. Its specific gravity was 6·77. We therefore conclude that this substance, although containing much hypobismuthic oxide, was not a pure salt.

2. In a paper by one of us, the preparation of hypobismuthic oxide has been described (this Journal, 1877, i, 28); we have somewhat modified that method, and have obtained good results. Bismuthous oxide is suspended in a large excess of potash solution of about 1·35 sp. gr.; the potash is kept nearly boiling, and chlorine is passed in until the precipitate is homogeneous, and of a dark chocolate-red colour; the precipitate is washed free from potash with hot water, kept in contact with dilute nitric acid (about 1 acid to 20 water) for 12 or 16 hours, until the colour of the solid has changed to brownish-yellow, washed free from acid, boiled for about an hour with a strong solution of sodium, or calcium, hypochlorite (preferably the former), till a perfectly homogeneous, yellow-brown, heavy powder is produced, which settles readily. This is washed with hot water till free from chlorine and alkali, and dried at 180—200° for two or three hours. A specimen thus prepared contained 86·81 per cent. of bismuth (mean of 86·54 and 87·08), and lost 3·17 per cent. when converted into bismuthous oxide by heating.

Bi_2O_3 requires 86·78 per cent. bismuth, and loses 3·30 per cent. on heating.

The prolonged digestion with nitric acid serves to dissolve any bismuthous oxide which may have escaped oxidation, and also to deoxidise the bismuthic oxide which has been formed; subsequent treatment with alkaline hypochlorite appears to convert any traces of bismuthous oxide yet present into hypobismuthic oxide.

3. The following method of procedure yields pure bismuthic oxide:—Bismuthous oxide is suspended in a large excess of very concentrated potash solution; specific gravity 1·37 to 1·38. The liquid is kept nearly boiling, and chlorine is passed in until the precipitate is quite homogeneous, and of a dark-red colour; the precipitate is then washed with hot water, until free from potash, and then with cold water, until every trace of chloride is removed; if any chloride is allowed to remain it is decomposed by the nitric acid subsequently added with formation of hydrochloric acid, which acts on the bismuthic oxide; it is then boiled for a very few minutes with concentrated nitric acid (whereby any remaining bismuthous or hypobismuthic oxide is removed) until all is distinctly scarlet, washed repeatedly and quickly with boiling dilute nitric acid, each quantity of acid being more dilute

than the preceding, and finally the acid is completely removed by washing with cold water; the scarlet precipitate is then dried at 125° for three or four hours.

A specimen thus prepared contained 83.87 per cent. bismuth (Bi_2O_3 requires 84.0 per cent.). Heintz (*Pogg. Ann.*, **63**, 559) recommends a method of preparation very similar to the above. Arppe states that anhydrous bismuthic oxide is obtained by the action of chlorine on bismuthous oxide suspended in *moderate excess* of strong potash solution. We have, however, failed (as Schrader did) to obtain the oxide by this process, the product being always a hydrated oxide, or mixture of hydrated oxides. Arppe does not state the temperature or conditions under which the salt which he obtained was dried.

We have attempted, but without success, to prepare oxides intermediate between bismuthic and hypobismuthic oxide (see Arppe, *loc. cit.*).

4. No hydrates of hypobismuthous oxide are known with certainty. Facts will be mentioned in the sequel which seem best explained by supposing that hydrates of this oxide are really formed during the oxidation of the oxide in presence of water.

About 0.5 gram of moist hypobismuthic oxide, prepared as described in par. 2, was placed over sulphuric acid for 12 hours; it then lost 6.5 per cent. on heating to 190 – 200° ; a portion of the same substance dried at 100° , lost 6.9 per cent. at 200° . The salt contained 81.16 per cent. bismuth. $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ requires 80.77 per cent. bismuth, and 6.92 per cent. water.

Thus the dihydrate, $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, is produced by drying the product of the oxidation of bismuthous oxide under the conditions stated in par. 2 over sulphuric acid, or at 100° . A similar result was obtained by Schrader, (*loc. cit.*).

Another specimen, after drying at 110° , lost 4.5 per cent. at 200° , which is rather more than the loss required by the monohydrate, $\text{Bi}_2\text{O}_4 \cdot \text{H}_2\text{O}$, viz., 3.59 per cent.

One of us has described the monohydrate, $\text{Bi}_2\text{O}_4 \cdot \text{H}_2\text{O}$, prepared by the action of chlorine in presence of aqueous potash on bismuthous oxide (this Journal, 1877, i, 28). The greater part of the hydrated oxide now prepared was a product of the deoxidation of $\text{Bi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$. It would appear that hypobismuthic dihydrate is produced by the deoxidation of hydrates of bismuthic oxide in presence of water, and hypobismuthic monohydrate by the oxidation of bismuthous oxide in presence of water, and under special conditions of concentration of potash, amount of chlorine used, &c.; probably, if the hydrate $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ be formed at an early stage of the process, the oxidised product is $\text{Bi}_2\text{O}_4 \cdot \text{H}_2\text{O}$; if $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ be produced, oxidation results in the formation of $\text{Bi}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (see paragraphs 8 and 9).

About 0.25 gram of hypobismuthic oxide was exposed to the action of ordinary and of moist air, with the following results:—

Hypobismuthic Oxide.

In air.				Over water.			
Gained	0.92	p. c. in	70 hours	Gained	8.98	p. c. in	70 hours
„	1.50	„	140 „	„	9.58	„	140 „
„	2.19	„	210 „	„	10.23	„	210 „
„	2.81	„	280 „	„	10.23	„	280 „

Bi_2O_3 to $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ requires 3.72 per cent. Bi_2O_3 to $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ requires 7.44 per cent. Bi_2O_3 to $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ requires 11.16 per cent.

In ordinary air the monohydrate is therefore slowly produced; but in moist air the oxide quickly passes into the dihydrate, and goes towards the trihydrate, but before this is completely reached deoxidation begins (see paragraphs 8 and 9).

5. The following results show the rate of hydration of bismuthous oxide; about 0.35 gram was used.

Bismuthous Oxide.

In air.				Over water.			
Gained	0.15	p. c. in	24 hours	Gained	1.83	p. c. in	24 hours
„	0.30	„	70 „	„	1.83	„	70 „
„	0.30	„	140 „	„	1.98	„	140 „

This oxide does not therefore take up a single molecule of water of hydration in moist air even after six days' exposure; in ordinary air only traces of water, probably hygroscopic, are assumed. The hydrates of this oxide are, it is well known, easily dehydrated; boiling with potash, or heating to a temperature below 100° , suffices to render these compounds anhydrous.

6. A quantity of moist bismuthic oxide, prepared as described in par. 3, after drying over sulphuric acid for seven days, lost 5.53 per cent. at 125° ; after four days' further drying, it lost 3.47 per cent., and contained 80.81 per cent. bismuth. $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ requires 81.08 per cent. bismuth, and 3.47 per cent. water. The salt was therefore bismuthic monohydrate.

The rate of hydration of bismuthic oxide is shown by the following numbers; about 0.5 gram was used:—

Bismuthic Oxide.

In air.				Over water.			
Gained	0.79	p. c. in	70 hours	Gained	3.36	p. c. in	70 hours
„	1.09	„	140 „	„	3.92	„	140 „
„	1.42	„	210 „	„	4.48	„	210 „

The monohydrate $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$, is therefore quickly produced in moist air, but the hydration scarcely proceeds further; in ordinary air, on the other hand, even after nine days, the oxide is only partially converted into the monohydrate. Bismuthic oxide, therefore, undergoes hydration rather less readily than hypobismuthic oxide; the hydration does not extend beyond a single molecule of water.

Bismuthic monohydrate also parts with its water of hydration at a lower temperature ($125\text{--}130^\circ$) than that at which hypobismuthic dihydrate is rendered anhydrous (160°).

When bismuthic oxide is repeatedly moistened with water, and allowed to remain in the air, or when it is placed in contact with a large excess of water, it undergoes deoxidation, with production of a noticeable quantity of the white hydrate, $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and also of a hydrate or hydrates of Bi_2O_4 .

The brown oxide Bi_2O_4 , after taking up rather more water than required to convert it into $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, began to appear whitish at the edges, and to lose weight slightly; showing that deoxidation was commencing.

Arppe (*loc. cit.*) states that bismuthic oxide does not take up water directly, but is converted into the monohydrate by the action of chlorine in presence of potash. Our experiments, we think, show that when exposed to moist air, this oxide does become hydrated; but inasmuch as the moist hydrate readily undergoes deoxidation, the best method of preparing the monohydrate is, undoubtedly, to proceed as described in par. 3, and to dry the product over sulphuric acid.

7. Boedeker (*Annalen*, **123**, 61) describes a brown salt, to which he gives the formula $\text{Bi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, prepared by the action of potassium cyanide on bismuth-nitrate solution. We have prepared Boedeker's salt and analysed it, with results which agree fairly with the formula $\text{Bi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. The properties of this salt are, however, so peculiar, that a fuller account of it is reserved for a future communication.

§. *Properties of Oxides and Hydrates of Bismuth.*

8. When moist hypobismuthous oxide is exposed in air, it rapidly undergoes oxidation to the white hydrate $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; when the dry salt is moistened with water and exposed in air, oxidation proceeds much more slowly. We explain these facts by supposing that hydrates of hypobismuthous oxide are produced during the drying of the moist substance, and that in the oxidation of the dried oxide, in presence of water, formation of a hydrate of Bi_2O_2 precedes that of the hydrate $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

An attempt to dry hypobismuthous oxide by heating in a current of carbonic anhydride did not give satisfactory results.

Hypobismuthous oxide, when kept in a stoppered bottle, very slowly passes into the white hydrate already mentioned. A quantity of the oxide so kept for three years had suffered oxidation to the extent of about 10 per cent.

The passage of Bi_2O_3 to $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ is attended with the evolution of a considerable quantity of heat; the oxidising substance is sensibly warm to the touch.

It has been already mentioned that bismuthic and hypobismuthic oxides, or the hydrates of these oxides, are partly deoxidised in presence of an excess of water, with production of $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. The deoxidation, especially of $\text{Bi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, is hastened by the action of direct sunlight. If a few drops of nitric acid be added to the water less deoxidation apparently occurs, but this seeming decrease is due to the solvent action exerted by the acid on the hydrates of bismuthous oxide which are produced.

9. The first product of the action of nitric acid on bismuthic oxide or hydrate is the hydrate $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Schrader): this has been fully confirmed. Thus a quantity of $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ was boiled with 1 : 1 nitric acid until all was of an orange-red colour, the residue was washed and dried at 160° . The brown salt thus produced contained 87.11 per cent. of bismuth, and began to give off oxygen at 230° . Bi_2O_4 requires 86.78 per cent. bismuth. Very dilute nitric acid does not, however, bring about this change, unless the time of action be very prolonged. Two portions, about 5 grams each, of pure $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ boiled with 100 c.c. water and 6 to 10 drops concentrated nitric acid, did not change colour, the residues when washed and dried over sulphuric acid, contained 81.47 and 82.2 per cent. bismuth, respectively, and 3.50 and 3.30 per cent. water. $\text{Bi}_2\text{O}_5 \cdot \text{H}_2\text{O}$ requires 81.08 per cent. bismuth and 3.47 per cent. water.

That dilute nitric acid exerts no oxidising action on hypobismuthic oxide is evident from the fact that portions of this oxide were not visibly changed when boiled with exceedingly dilute nitric acid, and that the residues, dried at 160° , contained 87.1 per cent. and 86.9 per cent. bismuth respectively. Bi_2O_4 requires 86.78 per cent. Somewhat more concentrated acid exerts a visible deoxidising action on Bi_2O_4 : this oxide dissolves in concentrated nitric acid and more slowly in concentrated sulphuric acid, with evolution of oxygen, and in hydrochloric acid with evolution of chlorine.

Hypobismuthous oxide is rapidly oxidised to the white hydrate of bismuthous oxide by a few drops of nitric acid; addition of a little more acid dissolves the hydrate formed; if a moderate quantity of acid be added directly to the oxide, part of it goes into solution as nitrate, and metallic bismuth simultaneously separates; $3\text{Bi}_2\text{O}_3 + 12\text{HNO}_3 = 2\text{Bi}_2 \cdot 6\text{NO}_3 + \text{Bi}_2 + 6\text{H}_2\text{O}$.

When hypobismuthous oxide was warmed with aqueous potassium permanganate, either alone or in presence of potash, the permanganate was reduced to manganate, and a dark brownish-red heavy substance was formed, which, after washing, dissolved slowly in concentrated nitric acid with evolution of oxygen, showing it to be Bi_2O_4 , or, more probably, a mixture of this oxide and Bi_2O_3 . Bismuthous oxide was not oxidised by boiling with aqueous permanganate; when potash was added and boiling was continued for some time, there was a very slight production of a higher oxide.

10. Arppe (*loc. cit.*) states that a red liquid, resembling dilute potassium permanganate solution and containing bismuth and potassium, is obtained by boiling bismuthic hydrate with potash.

Heintz (*Pogg. Ann.*, **63**, 559) says that Arppe conducted experiments in his presence, and that he obtained a liquid with a faint shade of green, and containing only traces of bismuth.

We have altogether failed to effect any change either in bismuthic or hypobismuthic hydrate by long-continued boiling with potash solution; the potash was all removable by washing with water.

In the preparation of these hydrates (by the action of chlorine on bismuthous oxide in potash) a red liquid is certainly produced, and if hydrochloric acid is added to this liquid, a reddish-white precipitate, containing bismuth and potassium, slowly separates. But we find that the colour of this liquid is due to small quantities of hydrates of the higher oxides suspended therein in an extremely finely divided state; if the red liquid be filtered through good paper, the filtrate is colourless, and contains neither bismuth nor potassium. We think that Arppe's so-called "potassium bismuthate" was a mixture of potash and hydrates of Bi_2O_4 and Bi_2O_3 , obtained from this liquid.

11. Some details of the action of heat on various oxides of bismuth have been already given in previous papers. The following results concerning this action, and also the action of oxygen, hydrogen, and carbon monoxide, show the reciprocal stabilities of the oxides of this element:—

In each experiment about 0.5 gram of the oxide was placed in a test-tube, carrying a cork and two tubes, one to deliver, the other to carry off the gas; the test-tubes were heated in a water-, paraffin-, or air-bath; the temperatures are approximate only, and may be regarded as correct within 5° . The test-tube and its contents were weighed at the end of each period noted in the tables; the course of reduction was therefore discontinuous.

Oxygen was purified by passing through potash, and then through boiled sulphuric acid; hydrogen, by passing successively through pumice soaked in potash and in silver nitrate, and finally through boiled sulphuric acid; carbon monoxide was stored in a gas-holder, and passed

through potash and boiled sulphuric acid before use. The gases were passed at approximately the same rate in each experiment; no special device was however adopted.

The temperature of initial action of carbon monoxide was determined by the method described by Wright (this Journal, Trans., 1878, 1).

Heating in air was conducted with the same arrangement of tubes, but *no current* of air was passed over the heated oxides.

Hypobismuthous Oxide.

On account of the difficulty of obtaining this salt perfectly free from bismuthous oxide and hydrates, we have only a few results to offer.

It has been previously shown that this oxide, when heated in an open vessel in air, begins to absorb oxygen at 180° (this Journal, 1877, ii, 136); we find that oxidation begins in oxygen at about 140° , and is complete at 240° , after ten minutes' heating; that reduction begins, and is rapidly completed in hydrogen at 300 — 310° , and begins in carbon monoxide at about 250° .

Bismuthous Oxide.

I. Temperature of Initial Action of Carbon Monoxide (about 0.5 gram taken).

Temp.	Time in mins.	Turbidity in baryta-water.
100°	4	none
150	4	none
200	4	very faint

Reduction in carbon monoxide begins therefore at about 200° .

II. Reduction in Hydrogen (0.553 gram taken).

Temp.	Time in mins.	Loss in mgms.	Percentage loss.
245°	15	4	0.72
255	10	1	0.18
300	10	8	1.45

Total loss = 2.35 per cent. Bi_2O_3 to Bi_2O_2 loses 3.44 per cent.

Reduction to Bi_2O_2 is therefore not complete in hydrogen at 300° after 35 minutes' (discontinuous) action.

Appearance of residue at 300° was black-grey mixed with yellow specks.

Bismuthous oxide is not altered by heating in air or in oxygen.

Hypobismuthic Oxide.

III. Reduction in Carbon Monoxide (0.247 gram taken).

Temp.	Time in mins.	Turbidity in baryta-water.	Loss in mgrms.	Percentage loss.
80°	4	none	—	—
90	4	none	—	—
95	4	none	—	—
100	4	very faint	—	—
115	4	decided	—	—
115	10	—	3.0	1.21
125	10	—	0.3	0.12
155	10	—	1.2	0.50
175	10	—	1.5	0.60
205	10	—	0.5	0.20
225	10	—	0.5	0.20
245	10	—	0.5	0.20

Total loss = 3.03 per cent. Bi_2O_4 to Bi_2O_3 loses 3.30 per cent.

Hypobismuthic oxide is almost wholly reduced to bismuthous oxide by heating in carbon monoxide at 245—250°; reduction begins at about 105°.

IV. Reduction in Hydrogen. No. 1. 0.459 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
215°	10	1.75	0.39
235	10	2.25	0.46

No. 2. 0.366 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
245°	10	4	1.09
255	10	1	0.27
265	10	21	5.74

Total loss (No. 2) = 7.10 per cent. Bi_2O_4 to Bi_2O_3 loses 6.61 per cent.

Appearance of residue was black, with a few greyish specks.

Hypobismuthic oxide is therefore reduced to hypobismuthous oxide in hydrogen at about 265—270° after 30 minutes' (discontinuous) action, but bismuthous oxide is not wholly reduced to the lower oxide in hydrogen, even at 300°. (See above, Table II.)

V. Heating in Air. 0.2592 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
245°	10	1.5	0.57
255	10	0.0	0.0
265	10	0.5	0.19
275	10	1.0	0.38
285	10	0.4	0.18
295	10	2.4	0.92
305	10	2.0	0.76
315	10	0.7	0.27
325	10	0.2	0.09

Total loss = 3.36 per cent. Bi_2O_4 to Bi_2O_3 loses 3.30 per cent.

Hypobismuthic oxide is therefore reduced to bismuthous oxide by heating in air to about 325°.

VI. Heating in Oxygen. 0.249 gram taken.

Temp.	Time in mins.	Loss. in mgrms.	Percentage loss.
245°	10	2.0	0.8
255	10	0.0	0.0
265	10	2.0	0.8
275	10	1.0	0.4
285	10	2.1	0.9
295	10	1.1	0.5
305	10	0.0	0.0

Total loss = 3.4 per cent.

Hypobismuthic oxide is therefore reduced to bismuthous oxide in a current of oxygen, at about the same temperature as that at which it suffers reduction when heated in air.

0.30 gram heated at 100° for 15 minutes, and then at 140° for 15 minutes, in a slow current of ozonised oxygen, underwent no change in appearance or in weight.

Heated to 200° in oxygen, no change of weight. Therefore this oxide is not oxidised by direct action of oxygen or of ozone.

Bismuthic Oxide.

VII. Temperature of Initial Action of Carbon Monoxide (about 0.5 gram taken).

Temp.	Time in mins.	Turbidity in baryta-water.
70°	4	very faint.
80	1	faint.

Therefore reduction begins at about 75°.

VIII. Reduction in Hydrogen. 0.5875 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
105°	15	5.0	0.86
125	15	2.0	0.35
145	15	3.0	0.46
165	10	1.5	0.26
205	10	3.0	0.46
215	10	3.0	0.46
255	10	19.5	3.32

Total loss to 215° = 2.85 per cent. Bi_2O_5 to Bi_2O_4 loses 3.2 per cent.

Total loss = 6.17 per cent. Bi_2O_5 to Bi_2O_3 loses 6.4 per cent.

Therefore bismuthic is almost wholly reduced to hypobismuthic oxide, at about 215°, and to bismuthous oxide at about 255°, by heating in hydrogen.

IX. Heating in Air. 0.5117 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
135°	10	0.0	0.0
145	10	2.1	0.4
155	10	1.0	0.2
165	10	0.5	0.1
175	10	1.4	0.3
185	10	0.0	0.0
195	10	0.0	0.0
205	10	0.0	0.0
215	10	1.0	0.2
225	10	1.5	0.3
235	10	1.4	0.3
245	10	3.4	0.7
255	10	5.7	1.1

Total loss = 3.6 per cent.

X. Heating in Oxygen. 0.5545 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
135°	10	0.5	0.1
145	10	1.1	0.2
155	10	0.5	0.1
165	10	1.2	0.2
175	10	0.8	0.15
185	10	0.8	0.15
195	10	1.8	0.3
205	10	2.1	0.4
215	10	0.0	0.0
225	10	0.5	0.1
235	10	1.1	0.2
245	10	3.8	0.7
255	10	7.8	1.4
305	10	8.4	1.5

Total loss to 255° = 4.0 per cent. Total loss = 5.5 per cent.

Bismuthic oxide heated in air to about 250° , or in a current of oxygen to about the same temperature, is therefore reduced to hypobismuthic oxide; heated in a current of oxygen to about 305° , it is almost wholly reduced to bismuthous oxide.

Heated in oxygen at 160° and at 200° under a pressure of 780 mm. bismuthic oxide suffered almost the same loss of weight as when heated under the ordinary pressure; therefore an additional pressure of 20 mm. mercury did not impress upon the oxide any greater stability than is possessed by it at the ordinary pressure.

12. We thought it advisable to examine the action of chlorine and bromine on the oxides Bi_2O_3 and Bi_2O_5 . One of us had previously found that chlorine acts on Bi_2O_3 to give BiCl_3 , and bromine (when heated with the oxide) to give $(\text{BiO})_{11}\text{O}_2\text{Br}_7$ (this Journal, 1877, 1, 24).

The oxides were subjected to the action of dry chlorine, and of dry carbonic anhydride charged with bromine vapour, in hard glass tubes. Action began between chlorine and bismuthic oxide as soon as the oxide was gently warmed; with bismuthous oxide action did not begin until a higher temperature was reached. Bromine did not act on either oxide so readily as chlorine; no distinct difference could be noticed between the readiness with which the bromine acted on the higher and on the lower oxide. The main product of the action of chlorine on bismuthous oxide was bismuthous chloride, recognised by its general properties and by estimation of bismuth; a very small quantity of the oxy-salt, $\text{Bi}_3\text{O}_4\text{Cl}_3$, already described as the product of the action of air, or nitrogen trioxide, on heated bismuthous chloride, was also formed. In the case of bismuthic oxide the products were the same, but a relatively larger quantity of the oxychloride was obtained. Bromine reacted on both oxides to form bismuthous bromide and the oxybromide formerly described as produced by heating together bismuthous oxide and liquid bromine, viz., $(\text{BiO})_{11}\text{O}_2\text{Br}_7$. Relatively more of the oxybromide than of the oxychloride was obtained; the deoxidising action of bromine on bismuthous and bismuthic oxides is therefore not so complete, under similar conditions, as that of chlorine.

13. The following data are given as approximate only. The specific gravities were determined by weighing in pure benzene, the specific gravity of which had been determined to be 0.881 (20°):—

Specific gravity at 20° of—

Bi_2O_4	= 5.60,	referred to water at same temperature.
Bi_2O_5	= 5.10	„ „
$\text{Bi}_2\text{O}_4.2\text{H}_2\text{O}$	= 5.80	„ „
$\text{Bi}_2\text{O}_5.\text{H}_2\text{O}$	= 5.75	„ „

PART II.—*On the Halogen Compounds of Bismuth.*

By M. M. PATTISON MUIR, G. BERNARD HOFFMEISTER, and C. E. ROBBS.

1. The only point with regard to the preparation of the chloride, bromide, or iodide of bismuth which we have to note is, that bismuthous iodide is very easily prepared in well-marked crystals by subliming together bismuth and iodine in proportions to form BiI_3 . Heintz prepared the salt by subliming the constituent elements in an atmosphere of dry carbonic anhydride (*Pogg. Ann.*, **63**, 55).

A sample of the iodide prepared by the direct union of the elements contained 35.44 per cent bismuth (theory requires 35.53). A specimen prepared three years ago, by Rammelsberg's wet method, now contained 35.31 per cent. bismuth (mean of 35.77 and 34.85 per cent.) showing that no decomposition had occurred.

An attempt was made to prepare Bi_2Br_4 by heating BiBr_3 in hydrogen; 0.5 gram of the salt lost only 3.6 per cent. at 220° , at which temperature sublimation of the original bromide proceeded rapidly (BiBr_3 to Bi_2Br_4 loses 17.7 per cent.).

Bismuthous iodide was heated in hydrogen, but no reduction occurred; the salt sublimed in hard steel-grey crystals, consisting of pure BiI_3 . One specimen contained 35.54 per cent. bismuth; another, which had been repeatedly sublimed in hydrogen, 34.63 per cent.; BiI_3 requires 35.53 per cent.

2. The action of hydrofluoric acid on bismuthous oxide results, according to Berzelius, in the production of bismuth fluoride, which is soluble in water, and separates therefrom as a white powder.

We heated bismuthous oxide with aqueous hydrofluoric acid in a platinum dish, replacing the acid as it evaporated. When action had apparently ceased the liquid was decanted and evaporated on the water-bath; we thus obtained a deliquescent, crystalline, greyish-white mass, which, after drying between filter-paper, contained 62.5 per cent. bismuth.

Another specimen prepared in this way, but dried by warming over a low flame for 6—8 hours, contained 65.37 per cent. bismuth (mean of 64.80 and 65.95 per cent.). $\text{BiF}_3 \cdot 3\text{HF}$ requires 64.22 per cent. bismuth. Another quantity of the same substance was heated in a closed platinum crucible till fumes of hydrofluoric acid were no longer evolved. The residue, which was a distinctly crystalline, grey, heavy powder, contained 79.2 per cent. bismuth (mean of 80.4, 79.0, and 78.1 per cent.). BiF_3 requires 78.65 per cent. bismuth. On boiling the deliquescent salt mentioned above with successive quantities of water, a heavy, white, non-deliquescent powder was obtained, which contained 86.50 per cent. bismuth; BiOF requires 85.71 per cent.

The greater part of the bismuthous oxide which was acted on by hydrofluoric acid remained as a heavy colourless powder; when this had been washed with cold water till the washings were nearly neutral, and dried at 100° , it contained 73.72 per cent. bismuth (mean of 74.0, 72.10, 73.40, and 74.42 per cent.). $\text{BiOF} \cdot 2\text{HF}$ requires 73.69 per cent. bismuth.

When washing of the insoluble in hydrofluoric acid had been continued, with hot water, till the washings were perfectly neutral—this required about 80 or 100 washings—the residual colourless powder dried at 100° contained 85.51 per cent. bismuth (mean of 85.70 and 85.31 per cent.). BiOF requires 85.71 per cent. bismuth.

Bismuthic fluoride was also obtained, in crystalline form, by very strongly heating the double salt $\text{BiOF} \cdot 2\text{HF}$, mentioned above, in a closed platinum crucible for about an hour. Closely agreeing numbers were obtained on analysis.

Bismuth fluoride, BiF_3 , is quite insoluble in, and is unacted on by water, is decomposed and dissolved by hot hydrochloric, sulphuric, or nitric acid, and is scarcely altered or volatilised by heating in an open platinum basin at a full red heat. The double salt $\text{BiF}_3 \cdot 2\text{HF}$ is slowly decomposed by cold, more quickly by hot water, with formation of $\text{BiOF} \cdot 2\text{HF}$. If a little free hydrofluoric acid be present in the wash water a considerable amount of bismuth goes into solution.

The final product of the action of aqueous hydrofluoric acid on bismuthous oxide is bismuthyl fluoride; bismuth fluoride is, however, much more stable towards water and towards heat than any of the other halogen compounds of bismuth.

3. It has been before shown that bismuthous iodide is much more stable towards oxidising agents and towards water than the corresponding chloride or bromide (this Journal, Trans., 1878, 192). The results of the experiments to be described exhibit this greater stability.

About 0.5 gram of bismuthous iodide was shaken up with cold water in the proportion of 3,000 mols. H_2O to 1 mol. BiI_3 for 30 and for 60 minutes, when the solution was filtered, and hydriodic acid determined in the filtrate:—

BiI_3 prepared in Wet Way.

Percentage decomposition after 30 minutes = 13.3

" " 60 " = 24.3

BiI_3 prepared in Dry Way.

Percentage decomposition after 30 minutes = 17.4

" " 60 " = 19.9

Under similar conditions BiCl_3 , or BiBr_3 , would be entirely decomposed to BiOCl , or BiOBr . The complete decomposition into BiOI , by

heating with water, of crystalline bismuthous iodide prepared "in the dry way" is much less readily effected than the decomposition of the iodide prepared "in the wet way."

The action of N_2O_3 on bismuthous chloride and bromide has been shown to result in the production of the oxy-salts $Bi_2O_2Cl_3$ and $Bi_2O_3Br_3$ respectively. About 5 grams of BiI_3 (prepared in the wet way) were heated in a **V**-tube in a current of dry N_2O_3 (prepared by heating starch with nitric acid). Action began before the salt sublimed, iodine was evolved, and a crystalline sublimate, which on examination and analysis proved to be BiI_3 , collected in the cold part of the tube and in a long attached exit-tube. About 0.3 gram (6.0 per cent. of the iodide used) of a red substance remained in the bend of the **V**-tube when the action was finished; this gave a slight red milkiness when boiled with water, but the greater part was unacted on; it contained 56.50 per cent. bismuth; $BiOI$ requires 59.50 per cent.

Bismuthous iodide is evidently much less fully decomposed by N_2O_3 than the corresponding chloride and bromide. The oxidised product of the action is $BiOI$, which is also produced by slowly subliming the iodide in air; no tendency to form complex oxyiodides corresponding to, or analogous with, the complex oxychlorides or bromides, appears to exist.

When sulphur is heated with bismuthous chloride, sulphobismuthyl chloride, ($BiSCl$), is produced. Bismuthous bromide and sulphur were heated in a subliming vessel in molecular proportions; much sulphur vapour was given off, crystals of bismuthous bromide sublimed, and a reddish crystalline mass remained, containing 47.44 per cent. bismuth and 51.30 per cent. bromine (mean of 47.17 and 47.60, and of 51.08 and 51.52 respectively), which does not differ much from the numbers required for $BiBr_3$, viz., bismuth 46.66, and bromine 53.53 per cent. The substance contained a little sulphur; it was readily decomposed by water, yielding a nearly white, apparently crystalline body, which contained 22.38 per cent. bromine and a little sulphur; $BiOBr$ requires 26.11 per cent. bromine.

These results show that bismuthous bromide is scarcely decomposed by sublimation in contact with sulphur, or if decomposed, that the sulphobromide formed is again easily resolved into its constituent substances; hence $BiSCl$ is a more stable salt than $BiSBr$, if the latter exists.

When bismuthous iodide and sulphur were heated together both substances sublimed unchanged; sulphur-vapour therefore has no action on vapour of bismuthous iodide.

The oxyhaloid salts of bismuth, as is usually the case, are more stable than the sulphohaloid salts. When dry sulphur dioxide is passed over hot bismuthous bromide no action ensues; it has been

before shown that neither is bismuthous chloride decomposed by this gas; it seemed unnecessary to make an experiment with bismuthous iodide, undoubtedly it would be unaltered by the action of hot sulphur dioxide.

No action is exerted by dry carbonic anhydride on heated bismuthous bromide.

4. It is stated in *Roscoe and Schorlemmer's Chemistry* that bismuthyl iodide when sublimed in air is resolved into a crystalline oxide. We find that only a very small quantity of this salt is decomposed, with formation of Bi_2O_3 , by heating even in an open vessel for some days.

5. Another attempt (see this Journal, 1877, 2, 136) was made, but only with negative results, to prepare a chlorobromide of bismuth by passing carbonic anhydride charged with bromine vapour over hot bismuthous chloride contained in one bend of a W-tube, the other limb being surrounded by a freezing mixture: no action occurred, the second limb contained liquid bromine only.

6. The final distribution of salts when bismuthous oxide is acted on by aqueous hydrochloric acid has been shown by one of us (No. II of these "Contributions") to be represented by the symbols on the right hand side of the equation—

We have now examined the distribution of salts which occurs when the same oxide is acted on by aqueous hydriodic acid, and find that it is not quite analogous to that just described; the reaction may be formulated thus:—

If, however, x be made very large relatively to the amount of HI present, if the temperature be raised, or if the changing system be exposed to the action of direct sunlight, BiOI is produced.

The reaction which occurs when aqueous hydriodic acid is added to bismuthyl chloride on the one hand, and aqueous hydrochloric acid to bismuthyl iodide on the other, may be thus expressed:—

The amount of change in a given time in the first reaction may be greatly decreased by adding a large quantity of water, whereby the BiCl_3 is reconverted as soon as produced into BiOCl: unless the value of x' be very large in this reaction little or no BiOI is produced. In the second reaction the course of the change may be modified by

making x' very large; the BiCl_3 produced is thus partly decomposed, and a secondary reaction occurs between the BiOCl thus produced and HI set free in the primary change, in accordance with the first of the two equations given above.

The actions which occur between the components of a system comprising BiCl_3 , BiI_3 , BiOCl , BiOI , HCl , HI , and H_2O mols., is thus seen to be very complex; the final equilibrium is conditioned chiefly by the relative quantities of the salts (largely the quantity of H_2O), and by the temperature: inasmuch as BiI_3 is more stable than BiCl_3 the iodide tends to be produced in relatively large quantities. Thermal measurements would undoubtedly throw much light on these phenomena of equilibrium: most probably the "heat of formation" of BiI_3 is greater than that of BiCl_3 , and the difference between the "heats of formation" of BiCl_3 and BiOCl greater than that between the "heats of formation" of BiI_3 and BiOI .

7. The following numbers are given as approximate only. The specific gravities were determined by weighing in benzene:—

Specific gravity of BiBr_3 at $20^\circ = 5.4$, referred to water at 20° .

"	"	BiOBr	"	= 6.7	"	"
"	"	BiOCl	"	= 7.2	"	"

Specific gravity of BiI_3 is given in text-books as 4.56, and of BiCl_3 as 5.65.