XII.—*On Certain Bismuth Compounds.* Part VI.

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1. IN part IV of the present series of papers I endeavoured to sketch a few of the general relations existing between the hydrates of bismuth and between these and the corresponding oxides. I incidentally mentioned a qualitative reaction of bismuthous oxide (Bi_2O_3) which, it seemed to me, was best explained on the hypothesis of the existence of hypobismuthous oxide (Bi_2O_2). In a short note, since communicated to the Society, I showed how the formation of this lower oxide of bismuth may be applied to the detection of very small quantities of the metal. I now propose to communicate some further details with regard to the preparation and properties of this lower oxide.

2. The history of the researches into the existence and nature of an oxide of bismuth containing less oxygen than bismuthous oxide (Bi_2O_3) is briefly as follows:—

Thomson (*Proc. Glasgow Phil. Soc.*, 1841–42, p. 4) mentioned the fact that a grey powder is formed when metallic bismuth is gently warmed in the air. He endeavoured to separate this powder from unoxidised metal by means of a sieve. Heintz endeavoured to prepare

an oxide of bismuth which should contain less oxygen than 3 atoms to 2 of metal by heating basic bismuth oxalate to 200° out of contact with air (*Pogg. Ann.*, lxiii, 55); by heating basic bismuth phosphate mixed with microcosmic salt in hydrogen (*ibid.*, lxiii, 559, *et seq.*), and by the attempted reduction of the trioxide in a mixture of carbon monoxide and dioxide (*ibid.*, lxiii, 559, *et seq.*). In the first case Heintz obtained what he believed to be a mixture of bismuth carbonate and metallic bismuth; in the second experiment metallic bismuth containing phosphorus was obtained, and in the third experiment no alteration ensued (see par. 3).

Schneider (*Pogg. Ann.*, lxviii, 49) attempted to prepare the wished-for oxide by reducing bismuth tartrate in hydrogen, also by reducing the double sulphate of bismuth and potassium in hydrogen. The results were in both cases unsatisfactory, although it appeared very probable that a suboxide of bismuth was produced.

Arppe (*Pogg. Ann.*, lxiv, 237) found that digestion of grape sugar and bismuth nitrate solutions, made alkaline with caustic potash, resulted in the production of what appeared to be a mixture of bismuthous oxide or suboxide and metallic bismuth. This experiment was repeated by Schneider (*Pogg. Ann.*, lxviii, 51), making use of a neutral solution of bismuth tartrate in place of bismuth nitrate; he found that metallic bismuth was alone produced. The observation of Berzelius (*Lehrbuch*, ii, 573), that a suboxide of bismuth is formed in the decomposition of water when the negative pole consists of metallic bismuth, does not appear to have been subjected to the test of sufficiently rigid experiment.

Vogel (*Kastner's Archiv.*, xxiii, 86), by digesting basic bismuth nitrate with excess of stannous chloride in closed vessels, obtained a black powder which readily burned to yellow oxide of bismuth when heated in air. According to Berzelius (*Lehrbuch*, ii, 574), this powder contained tin in addition to a suboxide of bismuth.

Schiff (*Ann. Chem. Pharm.*, cxix, 331, *et seq.*) examined more in detail the action of stannous chloride upon basic bismuth nitrate, and found that the first product is an ochre-coloured salt containing tin, bismuth, and oxygen; to this salt Schiff assigned the formula SnBi_4O_6 . When this compound was heated in air its colour changed to straw-yellow, and it now had the composition SnBi_4O_8 . Schiff also found that these tin salts might be produced by employing bismuthous oxide in place of the basic nitrate. When the first-named salt was treated with warm caustic potash-solution, in absence of air, Schiff found that the stannic oxide was withdrawn, while a black powder containing bismuth, but other than metallic bismuth, remained. The general reactions of this salt show that it was really hypobismuthous oxide.

Schneider (*Pogg. Ann.*, lxiii, 53, *et seq.*) showed that bismuthous oxide is transformed by the action of tartaric acid and caustic potash into a soluble double tartrate of bismuth and potassium (neither water nor caustic alkali causes a precipitate in neutral solutions of this tartrate); that from stannous oxide, by similar means, a double tartrate of tin and potassium may be formed; that these double tartrates react upon each other with the production of a salt containing bismuth, stannic acid, and tartaric acid, which is soluble in caustic potash; and that from this solution certain salts, especially sodium carbonate, sulphate, and chloride, throw down a precipitate consisting of $\text{SnBi}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$.

By using a solution of stannoso-stannic oxide (Sn_2O_3), in tartaric acid and caustic potash, in place of a similar solution of stannous oxide, and proceeding in a manner similar to that detailed above, Schneider obtained the salt $\text{Sn}_2\text{Bi}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$. Schneider found that hot caustic potash only partially withdrew the stannic oxide from these salts.

By preparing a neutral solution of potassium bismuth tartrate, and adding a dilute and slightly alkaline solution of stannous chloride in caustic potash, nearly neutralising excess of potash by means of dilute sulphuric acid, allowing the precipitate to settle out of contact with air, decanting the supernatant liquid, dissolving the precipitate in caustic potash, and removing tartaric acid by addition of sodium carbonate, Schneider obtained a black precipitate containing tin, bismuth, and oxygen, from which strong potash ley completely removed the stannic oxide, leaving pure hypobismuthous oxide. The last-mentioned series of reactions was carried out with cold solutions.

Finally, Schneider (*loc. cit.*) succeeded in preparing pure hypobismuthous oxide by dissolving 1 equiv. of bismuthous oxide along with 1 equiv. of stannous chloride in hydrochloric acid, pouring the solution into tolerably concentrated caustic potash, and washing the black precipitate so produced repeatedly with cold potash ley.*

3. I prepared a quantity of hypobismuthous oxide by the last-mentioned method of Schneider. The process is easily carried out. Care should be taken to conduct the washing with potash-solution in a stoppered flask which should be nearly filled with liquid.

The oxide was dried in a vacuum over sulphuric acid. It presented the appearance of a black, non-metallic, finely-crystalline powder. I did not find that this oxide takes up oxygen so readily as Schneider's account would lead me to suppose. When exposed to air in the moist state it slowly passes into the white hydrate, ($\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). When dried as described, hypobismuthous oxide is perfectly stable in the air

* I have entered into these historical details because I cannot find a clear account of the various methods of preparation of hypobismuthous oxide in any of the textbooks.

for a very considerable period. The following data give more exact information concerning the oxidation of the dry salt.

0.725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 160° for 3 hours, underwent no increase in weight.

0.725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 180 — 190° for 1 hour, gained 0.009 gram.

0.725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 180 — 190° for 3 hours, gained 0.0185 gram.

0.725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 180 — 190° for 5 hours, gained 0.0205 gram.

0.725 gram of the salt dried *in vacuo* over sulphuric acid, heated to 210 — 220° for $1\frac{1}{2}$ hours, gained 0.022 gram.

The amount of oxygen which 0.725 gram of Bi_2O_2 must absorb in order to be converted completely into Bi_2O_3 is 0.0266 gram.

Stating the above results in another way, we find that—

After being heated to 180° for 1 hour Bi_2O_2 absorbed 3.76 per cent. of the total oxygen required to convert it into Bi_2O_3 .

After being heated to 180° for 3 hours Bi_2O_2 absorbed 69.55 per cent. of the total oxygen required to convert it into Bi_2O_3 .

After being heated to 180° for 5 hours Bi_2O_2 absorbed 77.07 per cent. of the total oxygen required to convert it into Bi_2O_3 .

After being heated to 210 — 220° for $1\frac{1}{2}$ hours Bi_2O_2 absorbed 82.71 per cent. of the total oxygen required to convert it into Bi_2O_3 .

The colour of the oxide began to change very slowly at 180° ; at the close of the operation the great mass of the salt had assumed the light yellow colour of bismuthous oxide, but the outer layers were still for the most part only blackish-yellow. When hypobismuthous oxide is heated over a Bunsen-flame it is at once changed into bismuthous oxide. This change is not attended with any phenomenon which can be described as glowing or burning, which words have been used to describe the change by Vogel and others.

4. Hypobismuthous oxide is easily reduced to metallic bismuth by heating on charcoal in the inner blowpipe flame; the salt is likewise readily and completely deoxidised by heating in hydrogen or in carbon monoxide. Bismuthous oxide is also reduced to metal by heating in carbon monoxide: there appear to be some discrepancies in the statements made concerning this reaction. (See Gmelin's *Handbuch*, ii, 848, and Heintz, *loc. cit.*) Heated in carbon dioxide, hypobismuthous oxide is converted into a greyish-green powder which slowly passes into a yellow-green and finally into a yellow substance. The process is evidently one of slow oxidation.

5. The action of a tolerably concentrated boiling solution of caustic

potash upon the oxide results in the production of metallic bismuth. Hot dilute hydrochloric acid partially dissolves this oxide; the insoluble portion consists of metallic bismuth. Dilute sulphuric acid has a similar action; a much smaller quantity, however, of the salt passes into solution. Dilute nitric acid dissolves hypobismuthous oxide with great ease.

6. This oxide of bismuth is readily converted into the higher oxides by boiling with caustic potash and a little bromine; the final product of the reaction is bismuthic oxide, or rather hydrate, $\text{Bi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$. I find that the same reaction serves to convert bismuthous oxide, and even metallic bismuth itself, when finely powdered, into bismuthic hydrate. This method for preparing that salt is much easier and quicker than the ordinary method in which chlorine is used as an oxidiser. It is only necessary to heat bismuthous oxide with strong potash ley, to add bromine slowly, and finally to boil for a few minutes in order to obtain a good yield of the red hydrate. The product of the action is washed with water, warmed with concentrated nitric acid, and again washed free from acid.

I did not consider it necessary to perform a quantitative analysis of hypobismuthous oxide, inasmuch as there can be no doubt, from the general reactions of the salt, that the substance obtained by me was identical with that obtained by Schneider, who has given a large number of analyses all leading to the formula Bi_2O_2 .

7. In the fourth part of my papers on bismuth-compounds I have endeavoured to generalise some of the properties of the hydrates and oxides of bismuth, and to express these generalisations in appropriate formulæ. According to the formulæ therein given the passage from bismuthic to hypobismuthous oxide consists in a gradual drawing together of the bismuth atoms with simultaneous expulsion of oxygen atoms. I have shown that bismuthic oxide begins to suffer deoxidation at 150° , hypobismuthic oxide at 250° . It is known that bismuthous oxide is stable at a red heat; the fact that this oxide loses oxygen when heated in carbon monoxide, and also, as mentioned in part iv, when heated in an atmosphere of such reducing gases as are produced by the slow ignition of paper, shows that bismuthous oxide is more ready to part with oxygen than it is to pass into a higher state of oxidation. I have now shown that hypobismuthous oxide begins to absorb oxygen at a temperature of about 180° , but that the process of oxidation is slow at this temperature, also that this oxide parts with the whole of its oxygen without any great difficulty. The most stable oxide of bismuth is therefore evidently bismuthous oxide, Bi_2O_3 ; in this respect bismuth differs from phosphorus. The points of agreement and difference between the oxides and hydrates of the members of the nitrogen series is a subject of much interest. I

shall defer what I have to say upon this subject until I am in a position to discuss the general relations holding good between the members of the series.

8. I have already referred to the salts containing tin, bismuth, and oxygen obtained by Schiff and by Schneider. Schiff's salt, No. 1, has the empirical formula SnBi_4O_6 : I would suggest that very probably this substance is the dibismuthyl salt derived from that hydrate of tin which corresponds with the oxide SnO . When the salt is heated it absorbs oxygen and becomes SnBi_4O_8 ; this salt I would regard as the normal bismuthyl salt of the hydrate corresponding to stannic oxide (SnO_2). In the same way Schneider's salts may be viewed (1) as the normal bismuthyl salt of the hydrate $\text{Sn}(\text{OH})_2$; (2) as the acid bismuthyl salt of the hydrate, $\text{Sn}_2(\text{OH})_6$.

I have formulated these salts below—

Oxide of tin.	Bismuth salt.	Hydrate of tin.
SnO	Schiff's No. 1. $\text{Sn}(\text{OBi}_2\text{O}_2)_2$	$\text{Sn}(\text{OH})_2$

I have ventured to give the name of *dibismuthyl* to the group Bi_2O_2 when in combination—

Oxide of tin.	Bismuth salt.	Hydrate of tin.
SnO_2	Schiff's No. 2. $\text{Sn}(\text{OBiO})_4$	$\text{Sn}(\text{OH})_4$
SnO	Schneider's No. 1. $\text{Sn}(\text{OBiO})_3 \cdot 6\text{H}_2\text{O}$	$\text{Sn}(\text{OH})_2$
Sn_2O_3	Schneider's No. 2. $\text{Sn}_2(\text{OBiO})_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$	$\text{Sn}_2(\text{OH})_6$

9. In a paper communicated to the Society (*Chem. Soc. Jour.*, vol. ii, 1876, p. 12) I have shown that in the sublimation of bismuthous bromide, in a retort or other confined space of air, an oxybromide having the composition $\text{Bi}_8\text{Br}_6\text{O}_{15}$ is produced. If bismuthous chloride be slowly sublimed under similar conditions an oxychloride is produced; but this salt is not the analogue of the oxybromide just mentioned.

A quantity of bismuthous chloride was placed in a large watch-glass which was covered with another of the same size; the lower glass was very gently warmed during the space of about an hour. Well-defined crystals of the trichloride were obtained on the upper watch-glass, while a reddish-yellow highly crystalline powder remained in the lower. This powder was washed with water, whereby any undecomposed chloride was readily separated as BiOCl , the new oxychloride settling quickly to the bottom of the washing vessel: the residue was dried at $90\text{--}100^\circ$ and analysed—

(1)	0.519 gram	gave	0.467 gram	Bi_2O_3	=	0.4191	gram Bi.
(2)	0.519	„	0.469	„	=	0.4209	„ „
(3)	0.519	„	0.281	„	AgCl	=	0.06952 „ Cl.
(4)	0.519	„	0.283	„	=	0.0701	„ „

	Found.					Calculated for $\text{Bi}_3\text{Cl}_3\text{O}_2$.
	I.	II.	III.	IV.	Mean.	
Bismuth	80.73	81.09	—	—	80.91	81.98
Chlorine	—	—	13.39	13.51	13.45	13.86
Oxygen (by dif- ference)	—	—	—	—	5.64	4.16
					100.00	100.00

The results agree approximately with the formula $\text{Bi}_3\text{Cl}_3\text{O}_2$. I will give further analyses of the same salt in the sequel.

10. It is evident from this result, and from that already cited, that bismuthous bromide, when melted in presence of air, takes up a proportion of oxygen much larger than that which enters into combination with bismuthous chloride under similar conditions. The fact that the bromide is more readily oxidised than the corresponding chloride is also illustrated by the behaviour of hot bismuthous oxide towards chlorine and bromine respectively. The action of chlorine results in the formation of bismuthous chloride, that is to say, the chlorine exerts a deoxidising influence; the action of bromine results in the production of an oxybromide of bismuthyl, viz., $(\text{BiO})_n\text{Br}_n\text{O}_2$ (*Chem. Soc. J.*, vol. i, 1876, pp. 26—27). The greater readiness to take up oxygen exhibited by bismuthous bromide, as compared with the corresponding chloride, is in keeping with the general behaviour of the bromides and chlorides respectively.

11. Geuther and Michaelis (*Deut. Chem. Ges. Ber.*, iv, 76) have shown that the action of nitrogen trioxide or tetroxide upon phosphorous chloride results in the production of pyrophosphoryl chloride, $\text{P}_2\text{O}_5\text{Cl}_4$, and nitrosyl chloride, NOCl . Weber (*Pogg. Ann.*, cxxiii, 347) has described the properties of a compound of antimonious chloride and nitrosyl chloride, SbCl_3NOCl , obtained by treating the first-named salt with nitrogen tetroxide.

From a consideration of the formulæ and general behaviour of the bismuth chlorides, bromides, oxychlorides, and oxybromides, as compared with the corresponding phosphorus salts, I did not consider it probable that pyrobismuthyl chloride, $\text{Bi}_2\text{O}_3\text{Cl}_4$, would be formed by the action of nitrogen trioxide or tetroxide upon bismuthous chloride; it was more likely that oxidation would not be carried far enough to produce this salt.

A quantity of bismuthous chloride was heated to fusion in a small inverted retort, the beak of which was connected with a U-tube kept cool by being surrounded with a mixture of salt and ice. The vapours produced by heating together starch and moderately concentrated nitric acid were passed into the retort. So soon as the nitrous vapours came into contact with the fused mass, the latter appeared

to enter into violent ebullition; the retort became very warm; after a few minutes the contents of the retort had solidified to a reddish-yellow, compact, hard, crystalline mass. This mass was washed into a mortar, ground up with water, repeatedly washed with the same liquid, and finally dried at 90—100°. The washing with water showed that only a very small quantity of bismuthous chloride remained undecomposed after the reaction. The U-tube contained a quantity of a greenish-brown liquid, which, when mixed with water, gave the reactions for chlorine and nitrous acid: the liquid most probably contained nitrosyl chloride.

The salt dried at 90—100° was analysed.

- (1) 0.2658 gram gave 0.247 gram Bi_2O_3 = 0.2216 gram Bi.
- (2) 0.2658 " " 0.245 " " = 0.2199 " "
- (3) 0.8156 " " 0.744 " " = 0.6677 " "
- (4) 0.8156 " " 0.740 " " = 0.6641 " "
- (5) 0.2658 " " 0.145 " AgCl & 0.003 gram Ag =
0.0367 gram Cl .
- (6) 0.8156 " " 0.442 " AgCl & 0.0025 gram Ag =
0.1099 gram Cl .
- (7) 0.8156 " " 0.4475 " AgCl & 0.0015 gram Ag =
0.1110 gram Cl .
- (8) 0.8156 " after precipitation of bismuth as carbonate, required
48 cb.c. standardised silver nitrate solution for complete precipitation of chlorine = 0.1099 gram Cl .
(1 cb.c. AgNO_3 solution = 2.29 mgm. Cl).

	Found.					
	I.	II.	III.	IV.	V.	VI.
Bismuth	83.37	82.72	81.86	81.42	—	—
Chlorine	—	—	—	—	13.70	13.47
	VII.			VIII.	Calculated for	
				Mean.	$\text{Bi}_3\text{Cl}_3\text{O}_3$.	
Bismuth	—			82.34	81.98	
Chlorine	13.61			13.47	13.86	
Oxygen (by difference)	—			4.10	4.16	
				100.00	100.00	

12. The numbers obtained in the foregoing analyses, although agreeing very well with those required by the formula $\text{Bi}_3\text{Cl}_3\text{O}_3$, can, nevertheless, be interpreted by assigning one or other of the three following formulæ to the salt:—

	$\text{Bi}_4\text{Cl}_4\text{O}_3$.	$\text{Bi}_5\text{Cl}_5\text{O}_4$.	$\text{Bi}_7\text{Cl}_7\text{O}_6$.
Bismuth	81.51	81.30	81.01
Chlorine	13.78	13.24	13.69
Oxygen... ..	4.71	5.46	5.30
	100.00	100.00	100.00

Taking the mean of all the analyses of the salt, including those detailed in par. 9, we have the following result :—

Bismuth	81.86
Chlorine	13.53
Oxygen	4.61
	<hr/>
	100.00

These results agree equally well with the formula $\text{Bi}_3\text{Cl}_3\text{O}_2$ and with $\text{Bi}_4\text{Cl}_4\text{O}_3$.

If the salt has the composition expressed by the former formula, it may, perhaps, be regarded as *bismuthic bismuthyl chloride*, $\text{Bi}(\text{BiO})_2\text{Cl}_3$; if the composition expressed by the latter formula, as a compound of *bismuthous oxide* and *hypobismuthous chloride*, $\text{Bi}_2\text{O}_3 \cdot \text{Bi}_2\text{Cl}_4$; or as a derivative of bismuthous chloride in which chlorine is partly replaced by the group Bi_2O_3 , viz., $\text{Bi}_2 \left\{ \begin{smallmatrix} \text{Cl}_4 \\ \text{Bi}_2\text{O}_3 \end{smallmatrix} \right.$.

The reaction, $3\text{BiCl}_3 + 3\text{N}_2\text{O}_3 = \text{Bi}_3\text{Cl}_3\text{O}_2 + 6\text{NOCl} + \text{O}$, or

The reaction, $4\text{BiCl}_3 + 4\text{N}_2\text{O}_3 = \text{Bi}_4\text{Cl}_4\text{O}_3 + 8\text{NOCl} + \text{O}$,

may, perhaps, represent the production of the oxychloride from bismuthous chloride.

13. Whatever be the formula assigned to this oxychloride, the results of analyses, as well as the general properties of the substances, show that the salt produced by fusing bismuthous chloride in a confined space of air, is the same as that formed by the action of nitrogen trioxide upon the same chloride in the state of fusion. The oxidation is carried no further in the one case than in the other. In the case of phosphorous chloride, the result is different. This salt absorbs oxygen at a boiling temperature, giving POCl_3 , but is converted by N_2O_3 into $\text{P}_2\text{O}_3\text{Cl}_4$: in each case, the oxidation is more complete than with the corresponding chloride of bismuth, and the latter oxidation is more complete than the former.

14. The new oxychloride of bismuth is insoluble in, and is not acted upon by, water: exposed to the air for days, it undergoes no change: it is soluble in hot hydrochloric or nitric acid, but is less readily dissolved by hot sulphuric acid. When boiled with caustic soda solution, the whole of the chlorine is slowly removed and is found in the liquid, while a yellowish-white residue, free from chlorine, remains undissolved: this residue appears to consist of bismuthous oxide. When heated over the Bunsen lamp, the oxychloride suffers no change; at an incipient white heat it is fused to a yellowish pasty mass, while white fumes are evolved: the residue contains a considerable quantity of chlorine, and appears to consist for the most part of undecomposed oxychloride.

A quantity of the salt was gently heated in dry hydrogen; it readily underwent change, the colour first becoming reddish-brown, then black. The black salt appeared to preserve the crystalline form of the original substance: one preparation was found to contain 25·26 per cent. of chlorine, another, 9·16 per cent., and 85·1 per cent. of bismuth. The escaping hydrogen evidently contained suspended matter; when conducted into water, it produced a milkiness in that liquid, and after some time a white precipitate which contained bismuth and chlorine; the water simultaneously acquired a slightly acid reaction. The final product of the action of hydrogen upon this oxychloride is metallic bismuth.

15. In order to compare the action of nitrogen trioxide upon bismuthous chloride with that of the same substance upon the corresponding bromide, I submitted a quantity of the latter salt to the action of the fumes produced by heating starch with moderately concentrated nitric acid, under conditions exactly similar to those detailed in par. 11. The phenomena presenting themselves to the eye were very similar to those described in the paragraph referred to. A liquid was obtained in the U-tube, showing the reactions for bromine and nitrous acid. A light yellowish-grey, crystalline powder, which was unacted upon by water, was formed in the retort. Complete decomposition of the bismuthous bromide was effected by the nitrous fumes. The solid product of the action was washed with water, dried at 90—100°, and analysed.

(1) 0·2465 gram gave 0·1935 gram Bi_2O_3 = 0·1736 gram Bi.

(2) 0·648 „ „ 0·315 „ AgBr = 0·134 „ Br.

	I.	Found. II.	III.	Calculated for $\text{Bi}_3\text{Br}_6\text{O}_{15}$.
Bismuth	70·43	—	—	70·00
Bromine	—	20·68	—	20·00
Oxygen (difference)	—	—	8·89	10·00

The general behaviour of this oxybromide, as well as the results of analysis, leave no doubt of the identity of this salt with that produced by fusing bismuthous bromide in contact with air (*Chem. Soc. J.*, vol. ii, 1876, p. 12). Bismuthous bromide then resembles the corresponding chloride in the fact that the action of nitrogen trioxide upon the fused salt produces the same oxy-derivative as is formed by the action of air alone. With the bromide, however, the oxidation is, in each instance, carried further than is the case with the chloride.

16. An attempt to prepare an oxychloride of bismuth analogous to powder of Algaroth ($\text{SbOCl} \cdot 2\text{Sb}_2\text{O}_3$), by heating together bismuthic oxide, Bi_2O_5 , and bismuthyl chloride, BiOCl , led to negative results. A mixture of Bi_2O_3 and BiOCl only was obtained: the particles of the

two salts could be readily distinguished under a lens: the mixture was of indefinite composition.

17. Michaelis (*Deut. Chem. Ges. Ber.*, v, 9—414, &c.) has shown that phosphorous chloride forms with bromine a bromochloride having the formula PCl_3Br_2 : this compound is, however, very unstable, being resolved into free bromine and phosphorous chloride at 35° . The existence of this bromochloride is in keeping with the marked quinquivalent character of phosphorus. I have already described (*Chem. Soc. J.*, vol. i, 1876, p. 144) the unsuccessful attempts which I have made to prepare a chloride of bismuth containing more chlorine than bismuthous chloride. Keeping in mind the apparent fact that the quantivalence of an elementary atom is more or less influenced by the other atoms with which it is united in a molecule, I thought that it might be possible to prepare a bromochloride of bismuth in which bismuth should play the part of a quinquivalent element. Of course, the mere production of a compound having the composition expressed by the formula $n\text{BiCl}_x\text{Br}_n$, where $x + n = 5$, and where n is any whole number, would not enable us to determine the valency of bismuth. Nevertheless, having proved the actual existence of such a compound, the most simple hypothesis to explain that existence would, I think, be that which regards bismuth as a quinquivalent element.

One might, however, at the outset, almost despair of producing such a compound as that formulated above. Bismuthous chloride is solid at even somewhat high temperatures; it would scarcely be allowable to imagine the formation of a compound by the action of bromine upon the solid chloride: the compound, if produced, would most probably, almost certainly, undergo dissociation at temperatures considerably below the fusing point of bismuthous chloride: in other words, the compound would probably be dissociated before it was actually produced.

Actual experiments led only to negative results.

Bismuthous chloride was melted in a small bulb blown on the end of a long piece of glass tubing; bromine was added in the proportion required by the equation $\text{BiCl}_3 + \text{Br}_2 = \text{BiCl}_3\text{Br}_2$, and heating was continued until fumes of bromine nearly ceased to be evolved. The product was a greyish-white, crystalline, very deliquescent mass, which contained bismuth, chlorine, and bromine. Analyses of this substance varied somewhat in their results: thus, 65.47 per cent. of bismuth was found, 4.95 per cent. of bromine, and 30.12 per cent. of chlorine another portion showed 65.1 per cent. of bismuth, 2.88 per cent. of bromine, and 31.13 per cent. of chlorine. A portion of the substance was sublimed from one watch glass into another placed over it: the sublimate consisted of white deliquescent crystals, samples of which showed 65.81, and 64.39 per cent. of bismuth, with from 31 to 32 per

cent. of chlorine, and very small quantities of bromine. During the sublimation of the substance, a greyish, crystalline, non-volatile body was formed in the lower watch glass. Analysis, and general behaviour, showed that this was an oxychloride identical in composition with that described in pars. 9, 11, and 12. No bromochloride was produced in the above reaction: the results of analysis agree with the numbers demanded by bismuthous chloride, viz., bismuth 66.35, and chlorine 33.65 per cent.: the chloride evidently contained small varying quantities of mechanically adhering bromine.

18. In the sublimation of bismuthous chloride mixed with bromine, the former salt alone undergoes chemical change: that the bromine should be incapable of replacing chlorine when traces of oxychloride are once formed, was almost to have been expected; but it would not have been very remarkable had the presence of the bromine modified in some way the oxidising action of the air upon the fused chloride. No such modifying influence was however noticed.

19. All attempts to prepare trichloride of bismuthyl, BiOCl_3 , corresponding with POCl_3 , have failed. I imagined it might be possible to prepare the sulphur analogue, BiSCl_3 . In order to test the accuracy of this supposition, I very gently heated bismuthous chloride and sulphur, in the proportion of 1 molecule of the former to 2 of the latter, in a covered crucible for several hours. Colourless crystals, mixed with others of a yellow colour, were then apparent adhering to the lid of the crucible, while a dark-red crystalline substance was found in the crucible itself. This dark-red substance was unacted upon by water; it contained bismuth, chlorine, and sulphur. Estimations of chlorine gave results nearly agreeing with those required by the formula, BiSCl . The general properties of the salt were the same as those described by Schneider (*Pogg. Ann.*, xciii, 464) as characterising sulphobismuthyl chloride, BiSCl .

The direct action of sulphur upon bismuthous chloride results in the replacement of two chlorine atoms by one sulphur atom. Schneider (*loc. cit.*) has described other methods of preparing sulphobismuthyl chloride; he has also described (*Pogg. Ann.*, xciv, 628) the corresponding salt in which selenium is substituted for sulphur.