XVII. *On the Compounds of Tin and Iodine.* *By* Thomas H. Henry, *Esq.* *Communicated by* R. Phillips, *Esq., F.R.S.*

Received March 31,—Read June 19, 1845.

In a paper by Sir H. Davy, published in the Philosophical Transactions, 1814, he describes the compound of tin and iodine procured by heating these bodies together, out of the contact of air, as of a deep orange colour, fusible at a moderate heat, and volatile at a higher temperature.

The compound obtained by Gay-Lussac, by gently heating tin with twice its weight of iodine, and more recently by Rammelsberg, by the same method*, is described by them as a reddish-brown, transparent substance, yielding a powder of a dirty orange-yellow colour, and easily fusible.

A compound of tin and iodine was procured by Boullay†, by precipitating a solution of protochloride of tin with iodide of potassium, in slight excess.

The combinations procured by these methods have been considered to be identical in composition, although the compound procured both by Gay-Lussac and by Rammelsberg is stated by them to be decomposed by water, while the salt of Boullay is described by him as soluble in water without decomposition.

It will be seen, I think, from the following experiments, that the substance procured by heating tin with twice its weight of iodine, is a mixture of two salts, differing in composition, one of which is soluble in water to a slight extent, without suffering decomposition, while the other is immediately decomposed on bringing it in contact with water, the former being the real protiodide described by Boullay, and the latter a biniodide, a salt which has not yet, to my knowledge at least, been described, but which must have been the compound mentioned by Sir H. Davy, as it is of a brilliant orange colour, and sublimes at a temperature of 356° Fahr., while the protiodide, I find, may be heated to redness, out of the contact of air, without subliming.

100 grs. of tin, in a state of minute division, were mixed with 220 grs. of iodine, the mixture placed in a porcelain crucible well-covered, and sufficient heat being applied to fuse the iodine, violent action immediately took place, accompanied by the evolution of much heat and the sublimation of a portion of the iodine; when the action had ceased and the crucible had become cool, a brown transparent crystalline mass, weighing 310 grs., was removed from it; 10 grs. of iodine had been sublimed, therefore, by the heat evolved during the combination; upon breaking this mass, however, a button of metallic tin, weighing 45 grs., was found inclosed in it. This

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* Gmelin, Handbuch, vol. iii.

† Annales de Chimie, xxxiv. 372.

substance could not be the neutral compound, for the 210 grs. of iodine would require 98 grs. of tin to form the protiodide instead of only 55 grs.

The mass was therefore heated again in a Florence flask well-corked, with 45 grs. of tin in very fine powder, to replace the button removed from it, in order to ascertain whether the neutral compound could be procured by digesting this substance with the metal in a state more favourable to combination. The mass readily fused without any further action on the tin; but an orange-red sublimate was formed, condensing on the sides of the flask in brilliant acicular crystals. As the mass in the flask diminished in quantity, it became less fusible, until at length it required a degree of heat little short of dull redness to produce that effect, and then it ceased to give off vapour. The flask was now allowed to cool; when cold, it was cut, and the fused residue removed, which was found to weigh 86·5 grs. after the separation of 37·5 grs. of tin still uncombined.

This substance was of a deep red colour and crystalline texture, affording a powder of a bright red colour similar to that of minium; 50 parts of it were treated with strong nitric acid, which acted violently upon it, expelling iodine and leaving peroxide of tin, which weighed after ignition 22·1 parts =17·38 metallic tin =34·76 per cent.; a compound of one equivalent of tin = 59, and one of iodine = 126, would give 31·89 per cent. This excess in the quantity of tin arose from the heat employed in separating the two compounds, producing a portion of oxide by the decomposition of the protosalt, as will be seen further on. To ascertain the composition of the sublimate, 50 parts of it were decomposed by nitric acid, and gave 12·2 parts of peroxide = 9·597 metal =19·19 per cent.

100 parts, treated with a solution of pure carbonate of potash in slight excess, were decomposed, carbonic acid being evolved and peroxide of tin precipitated; the iodide of potassium produced was separated by alcohol, and after dilution with water, was treated with nitrate of silver; the precipitate dried and fused weighed 148·5=79·99 iodine. This gives

	Theory.		Experiment.
2 Iodine	=252	81	79·99
1 Tin .	= 59	19	19·19
	311	100	99·18

It was therefore a biniodide.

In the next experiment, I took one atom of each substance, viz. 59 grs. of tin and 126 grs. of iodine. The action was violent as before; there were 16 grs. of tin uncombined, and after the sublimation of the biniodide, the fused protosalt weighed 66 grs.; this was exposed to the air as little as possible during the process of sublimation, which being performed in a retort, less oxide was formed in consequence.

50 parts gave 21·1 peroxide of tin =33·2 per cent. metal. In order to ascertain the action of heat upon the protiodide of tin, I prepared some by precipitating a warm concentrated solution of recently prepared protochloride of tin, by a strong solution of iodide of potassium, in slight excess; the salt formed on cooling in beau-

tiful acicular crystals, which, after being washed with a little water, lost their lustre by drying at a very gentle heat.

50 parts gave 20·7 parts peroxide =32·36 per cent. tin ; 10 grs. of this were heated in a small tube, tightly corked, at first gently, and afterwards to complete fusion ; a little water condensed on the upper part of the tube with a minute portion of biniodide. When cold the tube was cut, the fused mass removed, and found to have lost 1·5 gr. ; it was slightly oxidized on the surface, and perfectly resembled the protiodide procured in the former experiments.

25·3 grs. of the same salt were heated to from 380° to 400° in an open porcelain crucible, a sublimate was produced, which was received in a paper cone, so placed on the crucible as not to prevent the access of air ; when no more vapour was given off, the crucible was cooled and weighed ; the residue was found to weigh 6·04 grs. ; it was ignited, and then weighed 5·91 grs., and was peroxide of tin. The sublimate, which was in small brilliant orange-red crystals, was biniodide of tin ; for 4·60 grs., decomposed with nitric acid and ignited, gave 1·115 peroxide = 19·06 per cent. of metal.

Now, supposing that two atoms of protiodide of tin had been decomposed, giving rise to one atom of periodide, and one atom of peroxide of tin, 25·3 grs. of protiodide should have left 5·13 grs. of peroxide, which is sufficiently near the quantity obtained to determine the nature of the decomposition. Berzelius states that the protofluoride of tin is converted, by the action of the atmosphere, into SnF^2, SnO^2 ; a decomposition exactly analogous to that above described.

I have not succeeded in obtaining a combination of tin and iodine corresponding to the sesquioxide, although Boullay conjectured that some yellow crystals, which he obtained on adding to a solution of protochloride of tin a solution of iodide of potassium, in which an additional half-atom was dissolved, were sesqui-iodide ; the crystals I obtained by this method were found to be pure protiodide.

On adding iodine to a solution of protochloride of tin, this salt suffers a remarkable decomposition ; if its solution be concentrated, an iodide of tin is precipitated, and a combination of chloride and iodide of the metal, in definite proportions, remains dissolved in the solution. If the iodine be added in excess, so that the solution acquires a brown colour, it yields crystals of biniodide on evaporation ; if, on the other hand, the protochloride be in excess, a portion of the protiodide is precipitated, and the remainder unites with protochloride of tin, in the proportion of one equivalent of each substance, and it remains dissolved in the solution of protochloride, but may be separated by evaporation in the form of delicate acicular crystals of a silky lustre, and straw-yellow colour.

On adding iodine to an equal weight of protochloride of tin, dissolved in a small quantity of water, I obtained some minute red crystals, which yielded on analysis

	Per cent.
Iodine	79·30
Tin	19·98
	99·28

it was the biniodide therefore; with 380 grs. of the protochloride of tin and 150 grs. of iodine, a precipitate was obtained, which was found to yield—

	Per cent.
Iodine	67·78
Tin	31·67
	99·45

it was therefore protiodide of tin.

The solution remaining after the precipitation of the protiodide was evaporated at a gentle heat, until sufficiently concentrated, and allowed to cool; some crystals were thus obtained which were freed as much as possible from the mother-liquor, by pressure in bibulous paper, but on attempting to purify them for analysis by redissolving them in water, they were immediately decomposed, giving a scarlet crystalline precipitate of protiodide of tin, while chloride of tin remained in solution; they were therefore pressed as dry as possible in bibulous paper, and afterwards retained *in vacuo* over sulphuric acid for some hours.

10 grs. were then treated with a solution of pure carbonate of potash, evaporated to dryness, redissolved in cold water and separated from the protoxide of tin by filtration; the solution acidulated with nitric acid, and the iodine precipitated by nitrate of palladium while hot, the precipitate washed, dried, and ignited, left 1·94 gr. of metallic palladium =4·586 grs. iodine. The chlorine was afterwards precipitated by nitrate of silver; the precipitate, washed, dried, and fused, weighed 5·22 grs.; upon dissolving the chloride of silver in ammonia 0·1 gr. of metallic palladium was separated, which had subsided with the chloride of silver as a subsalt; this leaves 5·12 for the true weight of the chloride of silver =1·263 chlorine; 5 grs. decomposed with nitric acid in excess, evaporated to dryness and ignited, gave 2·68 grs. peroxide of tin =2·108 of metallic tin.

This gives in 100 parts—

	Theory.		Per cent.	Experiment.
One atom chlorine	= 35·4	or	12·67	12·63
One atom iodine	=126	or	45·10	45·86
Two atoms tin . .	=118	or	42·23	42·16
	279·4		100·00	100·65

It is therefore a compound of one atom of protochloride of tin, and one atom of protiodide of tin.

The excess in the quantity of iodine in the above analysis, is probably owing to the tendency of the protonitrate of palladium to subside as a basic salt in company with precipitates, which is a great objection to its employment in analysis.

As the protochloride of tin is stated by GMELIN*, on the authority of BERZELIUS, to contain one atom of water of crystallization, while the late Dr. TURNER, in the last edition of his Elements, published during his life†, states that it contains three atoms

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* Handbuch, vol. iii.

† Edit. v. p. 550.

of water of crystallization, and several works of character do not give the composition of the crystallized salt at all, it became necessary to analyse the salt used in the above experiments; it was obtained by digesting strong hydrochloric acid with tin in excess at a moderate heat, and when a tolerably concentrated solution was obtained, decanting it and setting it aside to crystallize; the strongly acid mother-liquor was again digested with the tin and took up a fresh portion (it appears impossible to saturate hydrochloric acid with tin at once). The salt was in small prismatic crystals and dissolved in water, after drying on blotting-paper, forming a perfectly clear solution, and producing a great degree of cold; 700 grs. dissolved in 3 oz. of water reduced the temperature from 58° to 27° Fahr.

The crystals were coarsely powdered and pressed as dry as possible in bibulous paper; 25 grs. were dissolved in water acidulated by sulphuric acid, and the tin precipitated by sulphuretted hydrogen, the protosulphuret washed and dried, weighed 17·23 grs.; 16·2 of these were ignited in a porcelain crucible, and the ignition, repeated with a little carbonate of ammonia, gave 15·6 grs. of peroxide; this corresponds to 16·59 on the total quantity of sulphuret, which is equivalent to 13·09 of metal.

The excess of sulphuretted hydrogen was removed by a little sulphate of copper, and the chlorine, precipitated by nitrate of silver, gave 30·94 grs. of fused chloride of silver =7·72 chlorine.

To determine the water, 23·58 grains were retained *in vacuo* over sulphuric acid for twenty-four hours, and were found to have lost 3·87 grains = 16·41 per cent.; we have therefore—

	Experiment.	Theory.	Atom.	
Chlorine . . .	30·88	31·50	1	35·4
Tin	52·36	52·49	1	59
Water. . . .	16·41	16·01	2	18
	99·65	100·00		112·4

The following table contains the principal analytical results of this communication:—

Protiodide of tin . . .	SnI, solid and fixed, sparingly soluble.
Periodide of tin . . .	SnI_2, solid, volatile, decomposed by water.
Chloriodide of tin . . .	SnCl, SnI, solid, fixed, decomposed by water.

March 28, 1845.