XXI.—*On certain Polyiodides.*

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IN December, 1876, I read to the Chemical Society a paper in which I described the compound now known as triiodide of potassium. The graphic formula for this body, on the assumption that iodine is triatomic, may be thus represented, if its formula be taken as KI_3 :—

But, inasmuch as the compound HgI_6 is well known, it occurred to me that the triiodide of potassium might perhaps be more correctly represented as dipotassic hexiodide, with the formula K_2I_6 . In this case its graphic formula would be written thus:—

Now, if K_2I_6 be the true formula for the salt, it is evident that substitution-compounds might be obtained by displacing one atom of potassium with one atom of some other monatomic element, or perhaps of two atoms of potassium in K_4I_{12} by one atom of a diatomic element. With the view then to prepare some such substitution-compounds, I made the investigation whose results are now recorded.

The metal *silver* was first selected, as being monatomic, and having an iodide freely soluble in strong solutions of potassic iodide.

My first attempt was to make a solution containing silver, potassium, and iodine in the proportions required by the formula AgKI_6 . The iodides of silver and potassium were readily dissolved in the proportions indicated, and the boiling aqueous solution prevented from depositing crystals on cooling by the addition of a little alcohol; but, long before the required amount of free iodine had been dissolved, a large quantity of the silver was always precipitated as AgI , and this precipitate could only be dissolved by a further addition of potassic iodide. Moreover, the constituents of AgKI_6 could not be brought into solution together by first mixing them in the dry state, and then stirring with a small quantity of water.

Iodides of silver and potassium and free iodine were next dissolved in proportion to form $\text{AgK}_3\text{I}_{12}$. All the constituents were easily dissolved in a small quantity of water by the aid of heat, and nothing separated out on cooling. When this solution was allowed to evaporate slowly over sulphuric acid, crystals of argento-potassic iodide, slightly coloured by free iodine, first separated, next crystals of potassium triiodide, slightly contaminated with silver iodide, and, finally, crystals containing from 10 to 12 per cent. of argentic iodide and 53 per cent. of iodine, which was set free as vapour by the application of a gentle heat. The formula indicated by the analysis of these crystals is $\text{AgK}_3\text{I}_{12} \cdot \text{KI}$, which requires 12.27 per cent. of argentic iodide, 34.69 per cent. of potassic iodide, and 53.04 per cent. of iodine in excess over that contained in KI and AgI . Accordingly, a solution was made containing the above ingredients in the proportions mentioned. No argento-potassic iodide or potassium triiodide separated from this solution on evaporation; but three sets of crystals were removed from it, all having the same composition. The results of analysis are as follows:—

Analysis of Crystals II :—

The *iodine*, in excess of that contained in KI and AgI, was determined by titration with a standard solution of hyposulphite (thiosulphate) of soda, starch being used as an indicator.

- (a.) 0.292 gram required 11.7 c.c. of hyposulphite solution, of which 1 c.c. is equivalent to 0.0127 gram iodine.

This represents 0.14859 gram iodine, or 50.88 per cent.

- (b.) 0.345 gram required 13.8 c.c. of the above hypo-solution, equivalent to 0.17526 gram iodine, or 50.8 per cent.

Analysis of Crystals III :—

- (a.) 0.513 gram required 21.45 c.c. of hyposulphite solution, of which 1 c.c. = 0.01212 gram iodine.

This number is equivalent to 0.259974 gram iodine, or 50.67 per cent.

- (b.) 0.467 gram required 19.55 c.c. of the above solution of hypo, equivalent to 0.236946 gram iodine, or 50.73 per cent.

The mean of these numbers gives 50.77 per cent. of iodine in excess over KI and AgI.

In order to determine the silver iodide, a weighed portion of the compound was treated with a slight excess of solution of sulphurous acid gas, the yellowish liquid thus formed diluted freely with water, and the argentic iodide allowed to settle, collected on a weighed filter, washed, and weighed. The results were as follows :—

- (a.) 2.001 grams (Crystals II) yielded 0.234 gram AgI, or 11.694 per cent.

- (b.) 2.783 grams (Crystals III) gave 0.324 gram AgI, or 11.642 per cent.

The mean of these numbers is 11.668 per cent.

The *potassium* in the compound was estimated as *sulphate*. A weighed portion of the crystals was treated with sulphurous acid in excess, and the whole of the iodine precipitated by nitrate of silver. The argentic iodide was next removed by filtration, and excess of silver separated from the filtrate by hydrochloric acid and a second filtration. The clear liquid thus obtained was evaporated to a small bulk, mixed with dilute sulphuric acid, and evaporated to dryness. The residue thus obtained was treated with carbonate of ammonia, and ignited till its weight was constant.

- (a.) 3.718 grams (Crystals II) gave 0.642 gram K_2SO_4 , equivalent to 0.288193 gram K, or 7.75 per cent.

- (b.) 2.944 grams (Crystals III) gave 0.511 gram K_2SO_4 = 0.2293879 gram K, or 7.79 per cent.

The mean of these numbers gives 7.77 per cent. potassium. The *total iodine* contained in the salt was ascertained by addition of solution of sulphurous acid in excess, and precipitation by nitrate of silver, the argentic iodide being collected on a weighed filter, washed, and weighed. The results are as follow :—

- (a.) 5.123 grams (Crystals II) gave 7.812 grams of argentic iodide, equivalent to 4.222 grams iodine, or 82.41 per cent.
 (b.) 2.783 grams (Crystals III) gave 4.239 grams AgI = 2.291 grams I, or 82.32 per cent.

The mean of these numbers gives 82.36 per cent. of iodine. The *water* present was determined by deducting the amount of iodine in excess over KI and AgI , as determined by titration with hyposulphite, from the total loss which the crystals underwent when gently heated. The compound loses about half its water by efflorescence when dried over sulphuric acid, but may be dried without loss of water over chloride of calcium.

- (a.) 2.307 grams lost 1.266 grams by heat = 54.87 per cent., which leaves 4.21 per cent. H_2O .
 (b.) 2.555 grams lost 1.405 grams by heat = 54.99 per cent., leaving 4.33 per cent. H_2O .

The mean of the above numbers gives 4.27 per cent. H_2O . The formula of the potassio-argentic polyiodide determined from the above analyses is—

The concordance between the results of analysis and the requirements of the formula will be seen in the following table :—

	Theory.	Found.	
Iodine (total).....	82.33	82.36	{ 82.41 82.32
Potassium	7.8	7.77	{ 7.75 7.79
Silver	5.38	5.36	{ Mean of AgI determinations
H_2O	4.48	4.27	{ 4.21 4.33
	<hr/> 99.99	<hr/> 99.76	

	Theory.	Found.	
Iodine (free to act upon starch)	50.66	50.77	$\left\{ \begin{array}{l} 50.88 \\ 50.8 \\ 50.67 \\ 50.73 \end{array} \right.$
KI	33.13	33.007	$\left\{ \begin{array}{l} \text{Mean of two K} \\ \text{determinations.} \\ 11.694 \\ 11.642 \end{array} \right.$
AgI	11.72	11.668	$\left\{ \begin{array}{l} 11.694 \\ 11.642 \end{array} \right.$
H ₂ O	4.48	4.27	$\left\{ \begin{array}{l} 4.21 \\ 4.33 \end{array} \right.$
	<hr/> 99.99	<hr/> 99.715	

Though this salt is efflorescent when placed over strong sulphuric acid, it nevertheless deliquesces in the air. A small quantity of water dissolves it entirely, and it may be recrystallised from this solution by evaporation over sulphuric acid. The crystals occur in groups with a stepped arrangement; are almost black, with a peculiar lustre, and are very deliquescent. When treated with excess of water, iodine and argentic iodide are separated, whilst potassic iodide and some free iodine remain in solution.

The formula of the above compound might be written thus: $\text{AgKI}_6 \cdot \text{K}_2\text{I}_6 \cdot \text{KI} \cdot 5\text{H}_2\text{O}$, if we assume that the formula of the periodide of potassium is K_2I_6 ; one atom of potassium in K_2I_6 being displaced by one atom of silver; or the formula might be written thus, $4\text{KI}_3 \cdot \text{AgI} \cdot 5\text{H}_2\text{O}$, on the assumption that the salt is a *molecular* compound.

Seeing the close analogy between the metals potassium and thallium as regards their behaviour with iodine, each forming two iodides, in which the iodine appears to be of different atomicity, viz.:—

though, if the formulæ of the lower iodides be doubled, they, too, may be graphically represented, on the assumption that *I* is triatomic, thus:—

My next endeavour was to produce a compound between the periodides of thallium and potassium, having some such formula as $\text{K}_2\text{Tl}_2\text{I}_{12}$: in this, however, I was not successful, the only compound of potassium, thallium, and iodine, which appears to have a definite nature, being one which was discovered by Willm (*Jahresb.*, 1864, 251). I reproduced this salt and analysed it, but the results of my analysis point to a somewhat simpler formula than that proposed by

Rammelsberg (*Pogg. Ann.*, cxlvi, 592), viz., $3\text{KI} \cdot 2\text{TlI}_3 + 3\text{H}_2\text{O}$, whilst they have led me to adopt the same formula as the discoverer, viz., $\text{TlI}_3 \cdot \text{KI}$, except that I believe the salt to contain two molecules of water of crystallisation, my formula standing thus:—

The iodine in excess of that present as TlI and KI , and the water of crystallisation, were determined by the application of a gentle heat to a known weight of the crystals, and by weighing the residual iodides of potassium and thallium. The results are as follow:—

- (a.) 1.692 grams of the dried crystals lost 0.625 gram, or 36.93 per cent.
- (b.) 0.6475 gram lost 0.2385 gram, or 36.83 per cent.
- (c.) 2.8515 grams lost 1.052 grams, or 36.89 per cent.

The mean of the above determinations is 36.883 per cent.

The *thallious iodide* was estimated by washing the yellow mass, left after igniting the crystals, with boiling water upon a weighed filter, drying at 100°C ., and weighing the residual iodide of thallium.

- (a.) 0.6475 gram of the dry crystals gave 0.271 gram TlI , or 41.85 per cent.
- (b.) 1.872 gram gave 0.793 gram TlI , or 42.3 per cent.

Mean 42.105 per cent. Discrepancy due to sparing solubility of the thallious iodide.

The following analysis was made with a view to discover the relative proportions of potassium and thallium in the salt. The iodides of these two metals, left after igniting a known weight of the dried crystals, having been accurately weighed, were converted into sulphates by evaporating to dryness, after the addition of excess of dilute sulphuric acid; and the weight of the mixed sulphates was noted. 2.8515 grams of the dry salt gave 1.7995 grams of iodides of potassium and thallium after ignition. The weight of mixed sulphates obtained from these iodides was 1.228 grams. Now if the formula of the salt be, as I believe it is, $\text{KI}_3 \cdot \text{TlI} + 2\text{H}_2\text{O}$, or $\text{K}_2\text{I}_6 \cdot 2\text{TlI} + 4\text{H}_2\text{O}$, the above quantity of it would yield 1.226 grams of sulphates of thallium and potassium.

The thallium was precipitated from the aqueous solution of these mixed sulphates as basic chromate (Tl_2CrO_4), by the addition of solution of bichromate of potash and a slight excess of ammonia, and the chromate of thallium was collected and weighed.

0.937 gram of Tl_2CrO_4 was thus obtained, which corresponds with 0.7288 gram of thallium, or 25.55 per cent. The formula requires 25.91 per cent.; but this discrepancy is accounted for by the sparing solubility of the basic chromate of thallium.

The formula, $\text{K}_2\text{I}_6 \cdot 2\text{TlI} + 4\text{H}_2\text{O}$ requires—

	Theory.	Found.
I + H ₂ O	36.84 per cent.	36.883 { 36.93 36.89 36.83
TH	42.05 ,,	42.105 { 41.85 42.36

Of course there is no proof that the composition of the above salt is not $\text{ThI}_6 \cdot 2\text{KI} + 4\text{H}_2\text{O}$, for whether thallous iodide be dissolved in solution of potassium triiodide or thallic iodide (ThI_3) in solution of potassic iodide, the crystals which separate have the same form and composition, the only point worthy of notice being that the former solution is effected much more readily than the latter; but it seems clear that one of these two formulæ must be accepted in preference to those of Willm and Rammelsberg.

Before the isolation of potassium triiodide, Piffard (*Zeitschr. Chem. Pharm.*, 1861, 151) supposed that the solution of iodine in aqueous potassium iodide contained a definite periodide, because it gave a dark-coloured precipitate with a solution of acetate of lead, which precipitate, according to him, did not part with iodine to solvents.

On the other hand, Dosios a. Weith (*Zeitsch. f. Chem.*, 1869, 379) found that this dark precipitate did give up iodine to solvents, and hence regarded it as PbI_2 , mixed with free iodine, but did not analyse it. (See *Watts' Dict.*, 2nd Sup., p. 677.)

I obtained the above precipitate, collected it, washed it, and pressed it between blotting-paper. When dry, it appeared as a dark purple powder, which certainly imparted a purple tinge to carbon disulphide; but it seemed to me more important that it was constantly decomposed by washing, for lead could always be found in the washings, and its composition was variable.

It occurred to me, however, to employ a different solvent, viz., alcohol in the preparation of this compound. Accordingly I made a saturated solution of sugar of lead in boiling alcohol, and added it whilst hot to a strong alcoholic solution of potassium triiodide; a very slight precipitate (PbI_2) separated at once; the hot liquid was rapidly filtered, and deposited on cooling a number of small but well-formed crystals.

The salt thus formed is permanent in the air, i.e., it is not in the least deliquescent. It may be kept indefinitely in well-stoppered bottles without change, but it evolves the odour of iodine, and, if exposed, very gradually loses its lustre. The crystals appear to be square prisms, or elongated cubes, and are usually aggregated in clumps. By recrystallisation from hot alcohol, however, and gradual evaporation of the mother-liquor over sulphuric acid, I succeeded in obtaining some fairly large isolated crystals. Each crystal has six

faces, of which two (always opposite one another) have a dark purple reflection, whilst the remaining four reflect a greenish-golden light; they appear to be dichroic. The lustre is almost metallic; the crystals yield a dark-brown powder. When the crystals are dropped into water, they undergo no change in form, but the water is coloured faintly brown, just as it would be by free iodine; whilst the crystal loses its lustre and acquires a dull brownish appearance. The salt may be entirely, though slowly, dissolved in cold saturated solution of potassic iodide, ammoniac chloride, or ammoniac acetate. It also dissolves gradually in cold aqueous alcohol, but more readily in hot alcohol, from which it may be recrystallised easily.

The *specific gravity* of the compound could only be approximately ascertained, since no liquid could be found which was quite without action on the salt. By weighing in dilute sulphuric acid, which gave it a protecting coating, consisting chiefly of iodine and PbSO_4 , the number 3.084 was obtained.

The formula of the salt is somewhat complicated, as will be seen from the following results. The elements present are Pb, C, H, O, K, and I.

The *lead* was determined as sulphate.

(a.) 1.5408 grams of the dry crystals, treated with excess of sulphuric acid, evaporated to dryness, gave a residue which (after being digested with boiling water for some hours, washed with boiling water, and dried on a weighed filter at 100°C.) weighed 0.750 gram. This is equivalent to 48.67 per cent. PbSO_4 , or 33.249 per cent. Pb.

(b.) 0.7915 gram, dissolved in alcohol and water, diluted and precipitated with solution of sulphurous acid, the precipitate being washed and weighed as before, gave 0.384 gram of PbSO_4 , or 48.51 per cent., equivalent to 33.14 per cent. Pb.

The *carbon* was estimated as CO_2 by combustion with chromate of lead, the *hydrogen* being collected and weighed as water at the same time; rolled copper wire was employed to collect the vapour of iodine, which was plentifully evolved during the combustion with chromate of lead.

(a.) 0.5585 gram of the powdered salt gave 0.057 gram H_2O , and 0.176 gram CO_2 , equivalent to 0.0063 gram hydrogen and 0.048 gram carbon, or 1.112 per cent. hydrogen and 8.59 per cent. of carbon.

(b.) 1.673 grams gave 0.176 gram water, and 0.532 gave CO_2 , equivalent to 0.01844 gram hydrogen and 0.14509 gram carbon, or 1.1 per cent. of hydrogen and 8.67 per cent. of carbon.

The *potassium* was determined as *sulphate*. The powdered salt was mixed with pure oxide of copper and ignited, first gently, then strongly, till fumes of iodine ceased to be evolved. The resulting mass was digested in boiling water for many hours; and the turbid liquid

thus obtained was filtered and evaporated to dryness after the addition of sulphuric acid, bisulphate being converted into neutral sulphate by igniting the residue with ammoniac carbonate.

(a.) 3.3815 grams of the powdered salt yielded 0.35 gram. $K_2SO_4 = 10.35$ per cent., or 4.646 per cent. of potassium.

(b.) 2.307 grams of the recrystallised powdered salt gave 0.241 gram K_2SO_4 , equivalent to 10.446 per cent. of sulphate of potash, or 4.69 per cent. of potassium.

The *total iodine* present was ascertained by mixing a known weight of the dry crystals with excess of a solution of pure ferric chloride, free from Cl and HNO_3 (prepared by passing chlorine over red-hot iron filings), and submitting the mixture to distillation, the iodine being retained in a solution of potassic iodide, which was afterwards titrated with a standard solution of sodic hyposulphite, starch being used as an indicator.

(a.) 1.6908 gram Pb-salt gave a solution of I in KI, which required 54.5 c.c. of a solution of hyposulphite, of which 1 c.c. was equivalent to 0.1343 gram iodine. Hence 0.731935 gram iodine had sublimed over, or the compound contains 43.28 per cent.

(b.) 0.57 gram gave a solution which required 18.45 c.c. of the above hypo-solution, equivalent to 0.2477835 gram iodine, or 43.47 per cent.

The iodine contained in the salt, which was free to act upon starch, was estimated by dissolving known weights of the dry crystals in strong cold solution of acetate of ammonium, and titrating with standard hyposulphite.

(a.) 0.5397 gram, dissolved in aqueous acetate of ammonia, required 10.2 c.c. of hyposulphite solution, of which 1 c.c. = 0.01343 gram iodine. This is equivalent to 0.136986 gram iodine, or 25.38 per cent.

(b.) 0.2442 gram required 4.65 c.c. = 0.0624495 gram iodine, or 25.57 per cent.

Sulphates of Potassium and Lead.

The potassium and lead contained in the salt were determined together by first gently igniting a known weight of the crystals, to expel the iodine in excess over PbI_2 and KI, and to diminish subsequent loss by spiriting; and afterwards adding excess of dilute sulphuric acid and evaporating to dryness, the residue being carefully weighed.

(a.) 0.531 gram gave 0.316 gram of mixed sulphates, or 59.51 per cent.

(b.) 0.789 gram gave 0.469 gram of mixed sulphates, or 59.44 per cent.

The mean of the determination of K and Pb separately requires 58·987 per cent.

The empirical formula deduced from these analyses is

	Required.	Found.	
Pb ₈ = 1656	33·229	33·195	{ 33·249 33·14
C ₃₆ = 432	8·669	8·630	{ 8·67 8·59
H ₅₄ = 54	1·083	1·106	{ 1·112 1·1
O ₂₈ = 448	8·990	9·031	{ by differ- ence.
K ₆ = 234·6	4·707	4·668	{ 4·69 4·646
I ₁₇ = 2159	43·322	43·370	{ 43·47 43·28
<hr/>	<hr/>	<hr/>	
4983·6	100·000	100·000	

	Required.	Found.	
Free iodine (assuming that the salt contains 5KI ₃).....	25·43	25·46	{ 25·55 25·38
PbSO ₄	48·633	48·59	{ 48·67 48·51
Mixed sulphates	59·119	59·47	{ 59·44 59·51
K ₂ SO ₄	10·486	10·398	{ 10·446 10·35

The formation of a *rational formula* has at present baffled all my endeavours.