CLXVIII.—*The Trithionates and Tetrathionates of the Alkali Metals. Part I.*

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THE constitution and properties of the polythionates have been the subject of several papers recently published by various investigators, the principal being by A. Gutmann (*Ber.*, 1906, **38**, 1728, 3277; 1907, **39**, 509; 1907, **40**, 3614; 1908, **41**, 300, 1650), Julius Meyer and H. Eggeling (*Ber.*, 1907, **40**, 1351), Price and Twiss (Trans., 1907, **91**, 2021), and Colefax (Trans., 1908, **93**, 811); the last-mentioned had previously published papers dealing with the same subject (Trans., 1892, **61**, 176, 199, 1083).

Some time ago, we commenced the fuller investigation of the reaction described by one of us (Marshall, *J. Soc. Chem. Ind.*, 1897, **16**, 396), by means of which tetrathionate is produced by the interaction of persulphate and thiosulphate. The investigation has occupied more time than we anticipated, and the completion of it may be delayed; we therefore have thought it advisable to communicate now the results which have already been obtained.

The Constitution of the Trithionates and Tetrathionates.

The constitutional formula for tetrathionates proposed by Mendeléeff has been assailed by Gutmann, who assigns to these salts a "peroxidic" in place of a "persulphidic" structure, thus:

$$(MS_2O_2)O{\cdot}O(S_2O_2M)$$

in place of $(MSO_3)S{\cdot}S(SO_3M)$. It is unnecessary here to give a fuller statement of his views, seeing that a summary of them has already been given by Price and Twiss (*loc. cit.*). These authors show that certain results obtained by them are incompatible with Gutmann's assumption, which they reject in favour of the older view. In addition to the evidence which they bring forward, there are several other points which might be stated in favour of Mendeléeff's formula, and to which we desire to call attention.

In the first place, the occurrence of the reaction which has been referred to above as constituting the subject of the present investigation, would seem to contradict Gutmann's view. On the older assumption, the formation of tetrathionate in this action is quite analogous to the formation of persulphide along with sulphate by the interaction of sulphide and persulphate:

$$2MSM + (MSO_3)O{\cdot}O(SO_3M) = MS{\cdot}SM + 2(MSO_3)OM,$$

that is, the rupture of the peroxidic union in the persulphate is in each case associated with the formation of the much more easily effected persulphide union. On Gutmann's assumption, however, the rupture of the peroxidic union in the persulphate is associated with the formation of an exactly analogous peroxidic union in the tetrathionate, so that it is difficult to see why any such reaction should take place. The two views as to the nature of this reaction may be represented by means of the following equations:

$$2(MSO_3)SM + (MSO_3)O{\cdot}O(SO_3M) = (MSO_3)S{\cdot}S(SO_3M) + 2(MSO_3)OM.$$

$$2(MS_2O_2)OM + (MSO_3)O{\cdot}O(SO_3M) = (MS_2O_2)O{\cdot}O(S_2O_2M) + 2(MSO_3)OM.$$

Thiosulphate. Persulphate. Tetrathionate. Sulphate.

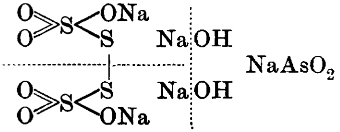
Further, if Gutmann's view were correct, the formation of tetrathionate by the interaction of iodine and thiosulphate would be of a very exceptional character, since peroxidic union cannot generally be brought about by means of iodine, but, on the contrary, iodine is liberated from iodides by the action of peroxides or analogous compounds.

As stated by Price and Twiss, of the various reactions studied by Gutmann, only two have any direct bearing on the question of the constitution of tetrathionates; the others are of too complex a nature to afford evidence for or against either of the constitutional formulæ under consideration.*

The first of these reactions is that of certain reducing agents, such as alkaline solution of arsenite, on tetrathionates. As observed by Gutmann, this action is represented by the following equation:

$$Na_2S_4O_6 + 8NaOH + 3NaAsO_2 = 2Na_2SO_3 + Na_3AsO_4 + 2Na_3AsO_3S + 4H_2O.$$

The striking point about the above reaction is the formation of arsenate in addition to monothioarsenate, seeing that it might have been expected that the function of the reagent in such a case would be to remove sulphur only. The fact that oxygen also is removed, forms the basis of Gutmann's argument for the peroxidic structure of the tetrathionate. The formation of arsenate can be explained very simply, however, without departing from the persulphide formula; it is only necessary to assume that the first action of the alkaline arsenite solution is, not to remove oxygen or sulphur from the tetrathionate, but to add sodium to it and so "reduce" it to thiosulphate, as illustrated in the following scheme:



or by the ionic equation:

$$S_4O_6'' + 2OH' + AsO_2' = 2S_2O_3'' + H_2AsO_4'$$
$$\text{or } S_4O_6'' + 4OH' + AsO_2' = 2S_2O_3'' + AsO_4''' + 2H_2O.$$

But as Gutmann has shown, thiosulphate is acted on by an alkaline solution of arsenite with formation of sulphite and monothioarsenate. The complete action is therefore represented as taking place in two stages: the first as above, and the second by the following equation:

$$4OH' + 2S_2O_3'' + 2AsO_2' = 2SO_3'' + 2AsO_3S''' + 2H_2O.$$

The following facts justify the above assumption as to the first action of the arsenite: (1) According to Spring (*Ber.*, 1874, **7**, 1161), sodium amalgam acts on tetrathionate to produce thiosulphate. (2) If hydrochloric acid is added to a mixture of arsenate and iodide, arsenious chloride and iodine are produced, but in the presence of alkali (car-

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* In a number of cases, Gutmann's results are open to grave objection from the fact that, for these experiments, he did not prepare his solutions from pure tetrathionate, but used directly the solution obtained by adding an equivalent quantity of iodine to a solution of a thiosulphate. Our experiments have shown that the presence of small quantities of other substances often has a very great influence on the decomposition of tetrathionates, and the solutions used by Gutmann in those particular experiments would necessarily contain at least a slight excess of either iodine or thiosulphate.

bonate), arsenite and iodine interact with formation of arsenate and iodide. Similarly, when hydrochloric acid is added to a mixture of arsenate and thiosulphate, arsenious chloride and tetrathionic acid are formed; it may therefore be surmised, in view of action (1), that probably here, also, the sense of the change will be reversed in presence of alkali, and that arsenite and alkali will form arsenate and thiosulphate.

The second reaction to be considered is that of alkaline cyanide solution on tetrathionate, which Gutmann shows to take place as expressed by the equation:

$$Na_2S_4O_6 + 2NaCN + 2NaOH = Na_2SO_4 + Na_2SO_3 + 2NaCNS + H_2O.$$

He, himself, makes no attempt to draw support for his formula from this reaction; as a matter of fact, his expectation was that the products would be sulphite, cyanate, and thiocyanate.

Gutmann states that the reaction takes place very slowly at the ordinary temperature, but this is not in accord with our experience. If a solution of tetrathionate is mixed with barium nitrate solution, and pure cyanide solution is added, the liquid remains clear only for a moment; a copious precipitation of barium sulphate and sulphite takes place almost instantaneously. The addition of alkali is not necessary, but if it is omitted, then twice as much cyanide has to be employed in order to complete the change:

$$Na_2S_4O_6 + 4NaCN + H_2O = Na_2SO_3 + Na_2SO_4 + 2NaCNS + 2HCN;$$

the presence of a great excess of hydrocyanic acid apparently does not affect the action.

In this case there is no need to assume the "reduction" of the tetrathionate to thiosulphate; the cyanide simply removes the two connecting sulphur atoms, leaving the two SO_3Na groups, which then interact with formation of sodium sulphate and sulphur dioxide, thus:

$$2SO_2ONa = SO_2(ONa)_2 + SO_2,$$

the sulphur dioxide would act either on the free alkali or, in its absence, on the cyanide, forming sodium sulphite. The formation of sulphate and sulphur dioxide from the two $NaSO_3$ groups would be to some extent analogous to one of the actions observed at the anode in certain electrolytic decompositions; for example, the formation of methyl acetate from two $CH_3{\cdot}CO_2{\cdot}$ groups during the electrolysis of an acetate solution:

$$2CH_3{\cdot}CO_2{\cdot} = CH_3{\cdot}CO_2{\cdot}CH_3 + CO_2.$$

The difference in the action of the alkaline arsenite solution and of the alkaline cyanide solution on tetrathionate is therefore easily explicable, using the persulphide formula, and is due to the preliminary formation of thiosulphate in the first case and not in the other.

The Interaction of Thiosulphate and Persulphate.

This action, as has already been shown (Marshall, *loc. cit.*), is expressed by the equation:

$$2M_2S_2O_3 + M_2S_2O_8 = 2M_2SO_4 + M_2S_4O_6.$$

In order to make use of this reaction as a means of preparing any particular tetrathionate, it is evident that a great advantage would be gained by using the thiosulphate of a metal which forms an insoluble sulphate along with the persulphate of the metal, the tetrathionate of which it is desired to obtain; in that case, if the proper proportions are employed, the resulting solution should contain the tetrathionate unmixed with other salt. In the first experiments, barium thiosulphate was used along with potassium persulphate:

$$2Ba_2S_2O_3 + K_2S_2O_8 = 2BaSO_4 + K_2S_4O_6.$$

Owing to the very sparing solubility of the barium salt, however, it was considered advisable to use, instead, the easily soluble strontium salt; this, notwithstanding its great solubility, can be obtained pure without much difficulty. The salt used for the experiments was prepared by fractional crystallisation from solutions of strontium nitrate and sodium thiosulphate. After three recrystallisations, the product gave, on analysis:

$Sr = 30{\cdot}39$.

$Sr_2S_2O_3,5H_2O$ requires $Sr = 30{\cdot}23$ per cent.

A moderate quantity of the persulphates of rubidium and cæsium being available, it was decided to make use of them for the preparation of the tetrathionates, seeing that these salts had not at that time been prepared. While the work was in progress, the paper by Meyer and Eggeling (*loc. cit.*) on the thiosulphates of these metals appeared. In it they described the preparation of the two tetrathionates by the action of iodine on the thiosulphates, the product being obtained from solution by the addition of alcohol. They thus obtained anhydrous, crystalline salts, which they analysed, but did not further describe. We had already obtained small quantities of hydrated crystals from purely aqueous solution, and saw no reason to discontinue our investigation.

The persulphates referred to above had been prepared by mixing a cold saturated solution of recrystallised ammonium persulphate with cold saturated solutions of rubidium chloride and cæsium sulphate respectively. In each case a sparingly soluble salt is precipitated, containing, however, some ammonium salt in isomorphous mixture. In order to get rid of this impurity, the salt was in the first instance recrystallised as rapidly as possible from hot water, and subsequently from hot water to which had been added a quantity of the appropriate hydroxide (or of barium hydroxide) sufficient to decompose the remaining ammonium persulphate.

Additional quantities of the salts had to be prepared later, and this was done either by the foregoing method or by double decomposition between ammonium persulphate and excess of the metallic hydroxide directly, in place of chloride or sulphate. When this method is employed, the ammonium salt must be added slowly to the hydroxide solution and not vice versa, otherwise the crystalline precipitate, which is first obtained, contains ammonium salt in isomorphous mixture.* The purified salts were analysed by conversion into the sulphate, and the results obtained in each case agreed closely with the numbers calculated for the anhydrous salt.

The reaction between persulphate and thiosulphate in solution takes place fairly rapidly, and is accompanied by considerable evolution of heat, so that to avoid decomposition due to rise of temperature, it is advisable to adopt some method of cooling the mixture. The method adopted was to place the materials in a long, narrow stoppered bottle, clamped to a wheel, which was rotated in a large vessel filled with cold water. It is desirable to avoid using excess of water to dissolve the reacting substances, since the somewhat unstable solution produced must subsequently be evaporated. In each case the quantity taken, whilst approximating to that required for the dissolution of the strontium thiosulphate, was not nearly sufficient to dissolve the persulphate, but was amply sufficient to retain in solution the tetrathionate produced. The precipitation of strontium sulphate may not begin until after the lapse of a minute or two, because of the increased solubility of the sulphate in presence of thiosulphate (compare Dobbin, *J. Soc. Chem. Ind.*, 1901, **20**, 218).

After several hours' agitation, the bottle was removed and allowed to stand until the precipitate had completely settled. The clear liquid was then poured off through a Buchner filter, after which the precipitate was transferred to the filter, drained as completely as possible, and then washed twice with very small quantities of water. The dissolved salt may be separated from the solution either by precipitation with alcohol or by evaporation at the ordinary temperature.

In the first experiments carried out in order to test the method, potassium persulphate was employed, and the tetrathionate was obtained without difficulty. When the method was next applied to the preparation of the rubidium salt, however, the yield of tetrathionate was not satisfactory. The solution behaved as if it were much less

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* Commercial potassium persulphate, being prepared by double decomposition from the ammonium salt, contains small quantities of this salt; it can easily be purified in the above manner.

stable than that of the potassium salt; a considerable quantity of sulphur was deposited from it, and the crystals which were obtained consisted mainly of trithionate. As it appeared improbable that there should be a marked difference in the stability of the salts, the exact conditions of the two experiments were reviewed, and it was found that in the second experiment the thiosulphate was in slight excess of the theoretical proportion, whilst in the first it was somewhat deficient Qualitative experiments were therefore made in order to find out if the decomposition of the tetrathionate might not be due to the presence of this slight excess of thiosulphate or its decomposition products (the solution becomes faintly acid). It was found that a pure solution of potassium tetrathionate at the ordinary temperature decomposes only slowly, with deposition of sulphur; the deposition of sulphur takes place more rapidly if a small quantity of thiosulphate, or of sulphurous acid, is added to the solution, and still more rapidly if both substances are added. The explanation of this is to be found in the observation made by Colefax (*loc. cit.*), that sulphite removes sulphur from tetrathionate with formation of thiosulphate and trithionate:

$$M_2S_4O_6 + M_2SO_3 = M_2S_2O_3 + M_2S_3O_6.$$

In a solution which, in addition to the above, contains free sulphurous acid, the action expressed in the following equation will take place:

$$M_2S_2O_3 + H_2SO_3 \rightleftharpoons M_2SO_3 + H_2S_2O_3.$$

This is not a stable equilibrium, however, since the sulphite will take up more sulphur from tetrathionate, and the thiosulphuric acid will decompose with deposition of sulphur and regeneration of sulphurous acid. The presence of thiosulphate and sulphurous acid together in the solution will therefore greatly accelerate the decomposition of tetrathionate in the direction of forming trithionate and liberating sulphur. In view of this fact, it is evident that a slight excess of persulphate must be used in the preparation of the tetrathionate. On the other hand, by using an excess of thiosulphate a satisfactory yield of trithionate may be obtained.

Before repeating the preparation of the tetrathionates of rubidium and cæsium in larger quantity, we decided to complete the investigation of the trithionates, and additional quantities of these were prepared, seeing that no description of the preparation and properties of these salts has yet been given. For the sake of completeness, we also re examined the potassium salt which has already been described.

Potassium Trithionate.

For the preparation of this salt, 20 grams of potassium persulphate, 46 grams of strontium thiosulphate (theoretically required: 42·4), and 70 c.c. of water were employed. The filtered solution soon became milky, and a yellow deposit of sulphur mixed with strontium sulphate gradually formed; the liquid was allowed to evaporate spontaneously in a current of air, and was filtered each day.

By the time crystals began to form, the tetrathionate was nearly all decomposed, and the solution was then allowed to stand until the mother liquor was reduced to a small volume. This was then removed as completely as possible, the crystals dissolved in the minimum quantity of water at about 30°, and the resulting solution filtered and allowed to crystallise. This purification was repeated until the solution no longer deposited sulphur when allowed to stand for two or three hours.

For analysis, the sulphur was determined by oxidation with bromine and precipitation with barium chloride:

0·3038 gave 0·778 $BaSO_4$. $S = 35·17$.

$K_2S_3O_6$ requires $S = 35·56$ per cent.

By the above method, the salt was obtained in thin prisms, which were not suitable for crystallographic measurements. In order to obtain better crystals, a solution saturated at about 30° was allowed to cool very slowly by leaving it for four to five days in a large, double-walled cylinder, the annular space of this vessel being filled with water at the same temperature; the cylinder itself was embedded in a box of sawdust. In this way considerably larger prismatic crystals were obtained, some attaining as much as 50 mm. in length and 4 mm. in breadth. Few of the crystals were entirely clear throughout; the larger ones always exhibited elongated cavities in the interior.

The density of the crystals was determined on selected fragments by the method of free suspension in a dense liquid (mixture of tetrabromoethane and xylene), using the Westphal balance.

Seven determinations gave results varying from 2·3335 to 2·3395. Mean value: $D = 2·336$. This differs considerably from the values given by Hertlein (*Zeitsch. physikal. Chem.*, 1896, **19**, 297), namely, 2·3044 and 2·3036. Probably Hertlein had not obtained sufficiently homogeneous material for his determinations. In order to make sure that our higher results were not due to the presence of some strontium compound, a quantity of the salt was prepared from potassium thiosulphate and sulphur dioxide, and the density determined on fragments of crystals grown as above. The result obtained was the same as before. The above value gives a molecular volume of 115·8.

The geometrical crystallography of potassium trithionate has been studied by various investigators; de la Provostaye (*Ann. Chim. Phys.*, 1840, [iii], **3**, 354), Rammelsberg (*Neueste Forschungen*, 1857, 27), and H. Baker (*Chem. News*, 1877, **36**, 203) all describe the salt as forming rhombic crystals which do not give very good measurements, owing to smallness or curvature of the faces; according to Rathke (*J. pr. Chem.*, 1870, [ii], **1**, 35), the crystals are monoclinic, but he did not actually perform any measurements.

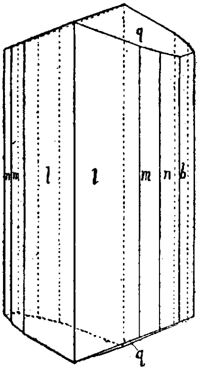
The data which we give were obtained with crystals grown as above-mentioned:

System and class: Rhombic bipyramidal.

$$a:b:c = 0{\cdot}7168 : 1 : 0{\cdot}4193.$$

Forms observed: $b = \{010\}$; $l = \{210\}$; $m = \{110\}$; $n = \{120\}$; $q = \{011\}$.

FIG. 1.



In addition to these, the form $k = \{031\}$ was occasionally observed, but it is always small. de la Provostaye mentions a pyramidal face

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$l : l = 2\bar{1}0 : 210$	7	39°18′—39°47	39°26′	*
$l : n = 210 : 120$	11	35 17 —35 48	35 29	35°23′
$l : m = 210 : 110$	5	15 27 —16 0	15 42	15 55
$m : n = 110 : 120$	6	19 36 —20 9	19 50	19 28
$n : b = 120 : 010$	6	34 43 —35 2	34 53	34 54
$q : q = 011 : 0\bar{1}\bar{1}$	10	45 23 —45 36	45 30	*
$q : b = 011 : 010$	10	67 11 —67 21	67 14	67 15
$q : k = 011 : 031$	1	28°46′	28 46	28 46
$k : b = 031 : 010$	1	38 29	38 29	38 29
$q : l = 011 : 210$	17	82° 3′—82°45′	82 25	82 30
$q : m = 011 : 110$	8	76 49 —77 5	76 57	76 59
$q : n = 011 : 120$	4	71 18 —71 27	71 26	71 30

$o = \{121\}$, but we did not observe this on any of our crystals. The faces of $\{011\}$ give very good reflections, but those of the vertical prisms are generally more or less curved and give poorer reflections; the faces $\{120\}$ are always narrow, and those of $\{010\}$ are frequently absent altogether.

No distinct cleavage.

When the crystals are examined through l in convergent polarised light, the interference figure seen indicates that the plane of the optic axes is parallel to $\{010\}$, with the axis c as acute bisectrix.

The refractive indices were determined by means of the total reflectometer, using the faces l and q. The values obtained are: $\alpha = 1{\cdot}4925$, $\beta = 1{\cdot}5646$, $\gamma = 1{\cdot}6014$ (Na light).

The axial angle calculated from these gives the value:

$$2V = 68^\circ\ 15'.$$

Rubidium Trithionate.

The method for preparing and purifying this salt is similar to that described for the potassium compound, but with different proportions of material. Twenty grams of rubidium persulphate require theoretically only 31·9 grams of strontium thiosulphate; it is therefore advisable to take about 33 grams, along with 40—50 c.c. of water. Rubidium trithionate appears to be decidedly more soluble than the potassium salt, but forms more perfect crystals; those used for examination were obtained by slow cooling, as before, and the largest measured about 25 mm. by 3 mm.

For the analysis, the sulphur was determined as in the previous case, and the rubidium was also determined by direct conversion into sulphate:

0·2800 gave 0·5428 $BaSO_4$. $S = 26{\cdot}63$.
0·1831 ,, 0·1811 Rb_2SO_4. $Rb = 47{\cdot}0$.
$Rb_2S_3O_6$ requires $S = 26{\cdot}52$; $Rb = 47{\cdot}05$ per cent.

The density, determined as before, was 2·845 as the average of seven determinations (limits, 2·843—2·847). Molecular volume = 127·7.

The crystals are isomorphous with the preceding salt, and are of a similar long-prismatic habit, although the forms observed are not all the same:

System and class: Rhombic bipyramidal.

$$a : b : c = 0{\cdot}7058 : 1 : 0{\cdot}4176.$$

Forms observed: $a = \{100\}$; $b = \{010\}$; $l = \{210\}$; $m = \{110\}$; $n = \{120\}$; $q = \{011\}$; $k = \{031\}$; $s = \{201\}$.

In addition to these, the form $o = \{111\}$ was also observed, but only on one crystal; it was not very small, however. The predominating forms are *m*, *q*, and *s*, the others being small and often incomplete.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$a : m = 100 : 110$	22	34°45′—35°25′	35° 3′	35°13′
$a : l = 100 : 210$	4	19 28 —19 38	19 33	19 26
$l : m = 210 : 110$	5	15 17 —15 59	15 44	15 46
$m : b = 110 : 010$	22	54 5 —55 18	54 59	54 47
$m : n = 110 : 120$	7	19 3 —20 5	19 32	19 28
$n : b = 120 : 010$	6	34 52 —35 25	35 12	35 19
$b : q = 010 : 011$	2	67 21 —67 22	67 21	67 20
$b : k = 010 : 031$	12	38 24 —38 55	38 37	38 36
$k : q = 031 : 011$	19	28 35 —28 52	28 43	28 44
$q : q' = 011 : 0\bar{1}1$	11	45 9 —45 26	45 20	*
$a : s = 100 : 201$	11	40 3 —40 23	40 12	40 12
$s : s' = 201 : \bar{2}01$	9	99 28 —99 45	99 36	*
$q : s = 011 : 201$	8	53 22 —53 30	53 26	53 26
$s : m = 201 : 1\bar{1}0$	5	51 7 —51 35	51 17	51 23
$a' : q = \bar{1}00 : 011$	1	90° 4′	90 4	90 0
$a : o = 100 : 111$	1	61 22	61 22	61 22
$o : q = 111 : 011$	1	28 36	28 36	28 38
$m : o = 110 : 111$	2	54° 2′—54° 3′	54 3	54 5
$o : m' = 111 : \bar{1}10$	1	101°14′	101 14	101 19
$s : o = 201 : 111$	1	27 11	27 11	27 17
$s : k = 201 : 031$	2	66°17′—66°21′	66 19	66 15
$m : k = 110 : 031$	2	63 31 —63 40	63 35	63 13
$m : q = 110 : 011$	6	77 13 —77 22	77 17	77 10

The optical character is similar to that of the preceding salt.

$$\alpha = 1{\cdot}4874,\ \beta = 1{\cdot}5580,\ \gamma = 1{\cdot}5867.$$

$$2V = 62°\ 33' \text{ (calculated).}$$

Caesium Trithionate.

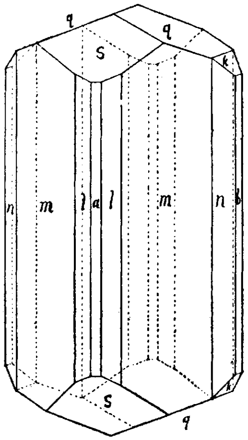
For the preparation of this salt, 32 grams of cæsium persulphate were taken along with 45 grams (theory, 40·4) of strontium thiosulphate and 60 c.c. of water; the purification, etc., were carried out as before. The salt is apparently still more soluble than the rubidium compound, but by evaporation at low atmospheric temperature, well-formed crystals with highly lustrous faces were obtained. When these crystals were removed from the mother liquor and dried on filter-paper, they rapidly became dull and opaque, indicating that the salt had been obtained in a hydrated form. This was confirmed by the analysis of fresh crystals. For the analysis, sulphur was determined as in the preceding case, and the cæsium remaining in the filtrate was determined as sulphate:

0·3090 gave 0·4554 $BaSO_4$ and 0·2340 Cs_2SO_4. S = 20·24; Cs = 55·65.
$Cs_2S_3O_6,H_2O$ requires S = 20·20; Cs = 55·87 per cent.

Using a mixture of methylene di-iodide and tetrabromoethane, the density was found to be 3·192, as the average of seven determinations (limits, 3·189 and 3·196). Molecular volume = 149·1.

A complete crystallographic examination could not be made at the time, owing to the rapid efflorescence of the crystals, but they were proved to belong to the triclinic system.

FIG. 2.



The easy dehydration of the salt indicated that the transition temperature is low, so that it might be possible to prepare the anhydrous salt in a crystallised form for comparison with those of potassium and rubidium. This was effected without difficulty by the very slow cooling of a hot solution (about 50°) containing alcohol. The salt is not isomorphous with the other two, however, but crystallises in the triclinic system. Since the crystals which were obtained were not very well formed, the crystallographic examination did not prove very satisfactory, and the description of both forms will therefore be deferred.

When it was sought to determine the density of the anhydrous trithionate, it was found that a whole crystal just floated on undiluted methylene di-iodide, but that after it was fractured, some of the fragments sank in the same liquid; the density would therefore appear to be very slightly higher than that of the methylene di-iodide, which we found to be 3·326.

For the analysis, the total sulphur was determined as before, and the cæsium directly as sulphate on a fresh portion :

0·2953 gave 0·4566 $BaSO_4$. S = 21·2.
0·1894 ,, 0·1532 Cs_2SO_4. Cs = 57·9.
$Cs_2S_3O_6$ requires S = 20·98 ; Cs = 58·07 per cent.

The Estimation of Rubidium and Caesium.

The estimation of the metals of the alkali group as sulphates by ignition with sulphuric acid is very simple in the case of the lowest member of the group, but becomes less easy with increasing atomic weight. This is due to the increasing stability of the acid sulphates and anhydrosulphates, and the increasing volatility of the normal sulphates. Various investigators have, on this account, recommended that rubidium and cæsium should be determined as acid sulphate or as anhydrosulphate by heating with sulphuric acid at some definite temperature, a method which is not very convenient. We have tried another method, which promises to give satisfactory results in a simpler manner. It was based on the fact that the metals of the alkali group form with those of the alkaline-earth group definite double sulphates of the type M_2SO_4,MSO_4, so that there was some reason to expect that if the ignition with sulphuric acid were carried out in presence of an excess of, say, calcium sulphate, the double salt would be formed in preference to the acid sulphate or the anhydrosulphate. In that case, the excess of acid might be completely removed at a temperature sufficiently below that at which appreciable volatilisation of the double sulphate would take place without the necessity of adhering to definite limits.

To test the method, a moderate quantity of pure calcium sulphate was placed in a platinum crucible, which was then ignited and weighed. As a preliminary test, which did not require to be repeated in subsequent experiments with the same material, sulphuric acid was added and the ignition repeated; there was no change in weight. The cæsium salt was next added along with sulphuric acid, and the whole gradually heated. It was found that a constant weight was attained at a low red heat, and that the increase in weight above that of the crucible and calcium sulphate alone agreed well with the quantity of cæsium sulphate calculated. The method would therefore appear to be satisfactory, but, as very few determinations have so far been made by means of it, a more extended test of its applicability still remains to be performed. The results of this we hope to communicate along with the other matters already foreshadowed.

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