L.—On Pentathionic Acid.

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THE doubts which are entertained respecting the very existence of pentathionic acid led us, at Dr. Roscoe's suggestion, to undertake the investigation of which we now give the results, prefacing the account however with a brief introductory sketch of such previous observations as enter most into the controversy and bear upon the salient points of the question.

Some years ago Kessler (*Pogg. Ann.*, **74**, 249) investigated the subject, and sought to confirm the existence of pentathionic acid in the solution obtained by Wackenroder's (*Ann. Chim. Phys.* [3], **20**, 144) original method, by means of a reaction with mercuric cyanide, which yields with this solution a reaction differing from that observed in the case of the other thionic acids. This difference consists in that, whilst with both tetrathionic and pentathionic acids free sulphur is liberated,

^{*} The question whether manganese dioxide forms manganites with the oxides of metals was discussed at some length before the Newcastle Chemical Society (*Chem. News*, **41**, 180) while the present investigation was being carried on.

with pentathionic acid twice as much of this element is set free as with tetrathionic acid. These reactions are illustrated as follows:—

- (1) $H_2S_2O_3 + Hg(CN)_2 + H_2O = H_2SO_4 + HgS + 2HCN.$
- (2) $H_2S_3O_6 + Hg(CN)_2 + 2H_2O = 2H_2SO_4 + HgS + 2HCN.$
- (3) $H_2S_4O_6 + Hg(CN)_2 + 2H_2O = 2H_2SO_4 + HgS + 2HCN + S.$ * (4) $H_2S_5O_6 + Hg(CN)_2 + 2H_2O = 2H_2SO_4 + HgS + 2HCN + 2S.$
 - $(4) 11_{2}S_{5}S_{6} + 11g(ON)_{2} + 211_{2}O = 211_{2}SO_{4} + 11gS + 211ON + 2S.$

Thus, mercuric cyanide decomposes all these polythionic acids in a manner very convenient for quantitative analytical determination. As a mean of many careful experiments, Kessler determined the quantities of sulphur, (a) in the sulphuric acid, (b) in the mercuric sulphide, and (c) the free sulphur formed. He thus obtained for the ratios a:b:c in the case of Wackenroder's solution, obtained by the action of SO₂ and H₂S in presence of water, the experimental numbers $2 \cdot 01: 1: 2 \cdot 08$. Now had the acid under examination been tetrathionic acid, the relationship must have been a:b::c=2:1:1, and this latter fact was practically demonstrated by similarly conducted analyses of the potassium tetrathionate.

In the course of last year (Ann. Chem. Pharm., 199 [1], 107) Spring made a critical investigation of the subject. Obtaining a solution of the acid by Wackenroder's method, he concentrated it by evaporation, and obtained a potassium salt, by first treating the ethereal solution of the acid obtained by shaking with ether, with pure alcohol, and then adding a dilute solution of potassium carbonate and shaking. The salt obtained dissolved in water according to Spring without leaving behind it the least residue of sulphur. It was deposited in small thin needles, and he states that the solution of these gave the reactions which are attributed to pentathionic acid. Spring's analyses of this salt undoubtedly prove it to be a tetrathionate. Hence Spring looks upon the existence of pentathionic acid as a myth, and endeavours to show in a variety of ways that all former observers have been mistaken, as they have had after all nothing but tetrathionic acid in their hands.

Next come experiments by Stingl and Morawski (J. pr. Chem. [2], **20**, 76–105), who give both qualitative and quantitative results, showing that an acid containing more sulphur than tetrathionic acid, really exists in the Wackenroder solution, and they draw attention to a qualitative reaction, by which pentathionic acid is clearly distinguished from any other of the thionic acids. They show, namely, that solutions of the alkaline and earthy hydrates immediately decompose this acid, with separation of sulphur. Alkaline carbonates effect the same decomposition, and even earthy carbonates slowly and on standing, the simple fact appearing to be that whilst the free acid is

* Pogg. Ann., 74, 265-274 (1848).

stable its salts are the very reverse. The precipitate of sulphur with the alkaline hydrates Stingl and Morawski found to be redissolved on boiling, with formation of polysulphides, easily detected with a drop of alkaline lead solution. The precipitated sulphur was also redissolved on standing, a portion being, according to the authors, first converted into alkaline sulphides, which dissolve more sulphur, with formation of thiosulphates. They represent the reactions which occur on treatment with potash, as follows:---

(I) $5(H_2S_5O_6) + 10KOH = 5(K_2S_4O_6) + 5S + 10H_2O.$ (II) $5(K_2S_4O_6) + 5S + 18KOH = 7K_2S_2O_3 + 6K_2SO_3 + K_2S_5 + 9H_2O.$

Stingl and Morawski further point out that free pentathionic acid is oxidised by potassium permanganate solution to trithionic acid without separation of a brown precipitate, and without addition of sulphuric acid. Tetrathionic acid is in like manner oxidised direct to trithionic acid, without precipitation. But setting out again with trithionic acid, even in presence of sulphuric acid, the first drop of permanganate causes precipitation at the ordinary temperatures, of a fine brown powder, of a manganese oxide. If now the solution obtained by Wackenroder's method, be titrated with permanganate till the brown colour appears, a considerably larger quantity of oxygen is needed, than would have been the case if a corresponding amount of tetrathionic acid had been present in solution. They also showed that with great excess of sulphuric acid and heating the solution, complete oxidation to SO₃ was effected, $H_2S_5O_6 + K_4Mn_4O_{16} + H_2SO_4 = 2K_2SO_4$ $+ 4MnSO_4 + 2H_2O$. The authors assert that the pentathionic acid solution decomposed by alkaline hydrates or carbonates as already mentioned, yields tetrathionic acid as a product, and add that this is proved by the fact that permanganate solution oxidises the filtered liquid in the cold. If a pentathionic acid solution be treated with calcium carbonate, calcium tetrathionate is said by them to be formed ; on standing, trithionate results, and finally calcium sulphate and sul-Stingl and Morawski also observed that on attempting to phur. titrate a pentathionic acid solution with potassium permanganate (the acid obtained by Wackenroder's method, and cleared of finely divided sulphur, by addition of CaCl₂ solution and filtering), too low results were obtained owing to separation of sulphur during the process of Oxidation with KClO₃ and HCl, and estimation of the sultitration. phuric acid formed, with barium chloride solution confirmed this. From these experiments the above-named authors give an affirmative answer to the question of the existence of pentathionic acid.

Very recently Kessler (Ann. Chem. Pharm., **200** [1 and 2], 256) combated Spring's views and conclusions, and Spring (*ibid.*, **199**, 118; also *ibid.*, **201**) in reply, asserts that the solution alleged to con-

tain pentathionic acid in fact consists of a solution of tetrathionic acid, together with some hyposulphurous acid, and that on removal of the latter acid, the solution gives with mercurous nitrate the following reactions :---

(I)
$$H_2S_4O_6 + Hg_2(NO_3)_2 = Hg_2S_4O_6 + 2HNO_3;$$

(II) $2(\text{Hg}_2\text{S}_4\text{O}_6) + 3\text{H}_2\text{O} = (\text{Hg}\text{S})_3\text{Hg}\text{SO}_4 + 2\text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_3 + \text{S}_4$

from which Spring concludes that only tetrathionic acid remains in the solution. He also asserts that this solution has the power of decolorising indigo, and concludes that the so-called and so-obtained pentathionic acid is nothing more than a mixture of tetrathionic and hyposulphurons (H_2SO_2) acids, the latter acid, as Schützenberger has shown, being the only sulphur acid known which possesses the power of decolorising indigo.

We commenced our own experiments by the preparation according to Wackenroder's method of a quantity of the so-called pentathionic acid solution, for the purpose of repeating the quantitative experiments of Stingl and Morawski and Kessler on the one hand, and of Spring on the other.

Hydrogen sulphide was passed into a saturated solution of sulphurous acid, until the smell of sulphur dioxide was no longer per-The precipitated sulphur obstinately passing through the ceptible. filter even after shaking the liquid with freshly precipitated metallic copper, a small quantity of freshly precipitated barium carbonate was added, and on immediate filtration a perfectly clear fluid was obtained. Though at first quite limpid, however, this filtrate gradually became turbid, from a slight decomposition of the sulphur compound formed. A current of CO₂ was then immediately passed through the solution in order to remove any sulphuretted hydrogen present in excess, the presence of which would account for the decomposition of the sulphur The solution was then warmed and again filtered from the acid. separated sulphur. This time the filtrate remained quite clear, and continued so permanently. The small quantity of barium present was removed by exactly sufficient dilute sulphuric acid, and the acid liquid concentrated by evaporation to about one-third of its bulk. The object of the first experiment, following Stingl and Morawski, was to determine the amount of sulphur in a known volume of the acid. This was calculated from the amount of oxygen expended by potassium permanganate in converting the thionic acid into sulphuric acid. It was further necessary to ascertain whether this amount of sulphur corresponds to the amount which should be found, if this acid really be pentathionic acid or any other, by comparing the total sulphur independently estimated in a similar volume of the acid solution. For this purpose 10 c.c. of the acid solution were taken and acidified with

an excess of dilute sulphuric acid, and then titrated with the permanganate solution, of which each c.c. = 0.00164 gram of available oxygen. If the operation were conducted in the cold, a brown precipitate was formed, which rendered it impossible to observe the end of the reaction. It was therefore necessary to heat the acidified solution and conduct the process exactly as described by Stingl and Morawski.

		Mean.		120.1	.,		
10 c.c.	,,	,,	,,	120.0	,,	"	,,
10 c.c.	"	,,	"	120.0	,,	,,	,,

Hence $120\cdot1 \times 0.00164 = 0.19696$ gram of oxygen was needed for the complete oxidation to sulphuric acid. Now if this solution contained pentathionic acid (H₂S₅O₆), the amount of sulphur corresponding or equivalent to the oxygen required for the complete oxidation, would be also 0.19696 gram, whereas, if the solution merely contained tetrathionic acid (H₂S₄O₆), the amount of sulphur would be 0.19696 × $\frac{8}{7} = 0.2251$ gram. The reason for this we will now show.

A molecule of tetrathionic acid requires less oxygen for its complete oxidation to sulphuric acid than a molecule of pentathionic acid does. Consequently, for the same amount of oxygen actually required, the number of molecules present in the case of tetrathionic acid must be greater, and contain a larger amount of sulphur than if pentathionic acid alone were present. The ratio of the weight of oxygen to that of sulphur required for complete oxidation, is that of equality in the case of pentathionic acid, whilst it is as 7:8 in the case of tetrathionic acid. This is evident from a consideration of the following equations:—

I.
$$\begin{cases} H_2S_5O_6 + O_{10} = H_2O + 5(SO_3), \text{ hence } S = 32 \times 5 = 160 \\ O = 16 \times 10 = 160 \end{cases}$$

II.
$$\begin{cases} H_2S_4O_6 + O_7 = H_2O + 7(SO_3), \text{ hence } S = 32 \times 4 = 128:8 \\ O = 16 \times 7 = 112:7 \end{cases}$$

The total amount of sulphur actually present in the acid solution, was determined by previously oxidising the solution with potassium chlorate and hydrochloric acid, and then precipitating as barium sulphate.

From 10 c.c. of the acid solution-

	Ι.	II.
BaSO ₄ obtained	1.6188 gram.	1.6184 gram.
Corresponding to S	0.2223 ,,	0.2222 ,,
S deduced from oxygen, required for $H_2S_5O_6$	By titration	0.19696
S deduced from oxygen, required for $H_2S_4O_6$	f permanganate	0.2251

But Stingl and Morawski observed that some sulphur is separated during titration, and hence too low a number is obtained. Stingl and Morawski state that this separation of sulphur is due to a decomposition of the tetra- and tri-thionic acids formed, in titrating with permanganate in presence of much sulphuric acid. We found that the end of the reaction was almost impossible to hit, owing to the dark colour acquired by the solution, and we cannot therefore attach much importance to the above numbers obtained, or to the process.

A determination was now made by Kessler's method, by estimating the amounts of sulphuric acid, mercuric sulphide, and free sulphur obtained by the action of mercuric cyanide on the freshly prepared acid solution obtained by Wackenroder's method. For this purpose 10 c.c. of the solution were taken and boiled with an excess of mercuric cyanide till the yellow precipitate, which was at first formed, became black. The mercuric sulphide containing free sulphur was then thrown on to a weighed filter, dried at 100° , and weighed. The whole was then treated with strong nitric acid, with addition of potassium chlorate to oxidise the sulphur completely to sulphuric acid, which was estimated as barium sulphate. From the latter the total sulphur was calculated, and this deducted from the contents of the weighed filter dried at 100° (mentioned above) gave the mercury, from which the sulphur as sulphide was at once deduced, leaving that which was in the free state.

Thus, then, the following results were obtained :---

Mol. weight. Mol. ratios. $H_2SO_4 = 0.3929 \text{ gram} \div 98 = 0.00390 : 2$ = 0.4549HgS $\div 232 = 0.00196 : 1$ = 0.1227S 32 = 0.00383 : 1.95÷ ,, Amount of sulphur in the H_2SO_4 formed = 0.1283 HgS= 0.0627,, Free sulphur = 0.1227Total sulphur = 0.3137

The total sulphur was estimated independently by oxidising the acid solution with potassium chlorate and hydrochloric acid. Thus from 10 c.c. of the solution 2.3383 grams of BaSO₄ were obtained, which

gives 0.3211 gram of total sulphur as against the number 0.3137 gram deduced from the data yielded in the former experiment by Kessler's method. This experiment indicates that the solution contained pentathionic acid, for in the case of tetrathionic acid the ratios of H_2SO_4 , HgS, and S ought to be 2:1:1, whereas we, like Kessler, obtain the relation 2:1:2 practically.

Decomposition of the Wackenroder Solution by Alkaline and Earthy Carbonates and Hydrates.

Stingl and Morawski observed, as already stated, that by the action of alkaline and earthy carbonates on the pentathionic acid solution, thiosulphuric acid is formed and sulphur deposited. But the most characteristic reaction for pentathionic acid is the one with caustic alkalis and consequent precipitation of sulphur, upon which stress was laid by Stingl and Morawski. Lime-water has a similar effect, and we find that the addition of ammonia solution even causes precipitation after a few seconds. To a solution of the acid, magnesia was added in fine powder. The magnesia dissolved, when the acid was in excess, to a clear solution, remaining clear for a considerable time. On adding excess of magnesia, however, and then attempting to redissolve by adding excess of the acid solution, the magnesia was dissolved, but a white precipitate of sulphur remained. Spring appears to doubt that the precipitate formed in such a case as this does entirely consist of sulphur. This point we have frequently proved by collecting the precipitates formed, washing, drying, and carefully heating in the flame, when the residue burns with a blue flame, smells of SO₂, and leaves no residue.

Now in all cases the precipitate of sulphur formed by the action of caustic alkaline solutions in excess on the acid Wackenroder solution, after standing for some hours completely redissolves. If the precipitate with solution be boiled, the former is almost immediately redissolved, and sulphides or polysulphides are formed, and then a black precipitate is produced with a few drops of an alkaline lead solution. The solution in which the sulphur has redissolved on standing merely, does not precipitate lead solution black. The two following experiments show that not only the excess of alkaline hydrate, but also the decomposition products of the pentathionic acid, play a part in the re-solution of the sulphur :—

(I) On cautiously adding acid to the sodium hydrate solution containing the precipitated sulphur, till neutrality was attained, on standing, re-solution of the sulphur does *not* take place.

(II) On letting the freshly precipitated solution stand till the sulphur has settled down (hastened by first shaking the liquid), and then

washing by decantation with water, till the finally decanted liquid was no longer alkaline to test-paper, when excess of caustic soda solution was added, solution of the sulphur did not occur after standing for three days. (If not washed thus, standing for 4-5 hours would have been sufficient for re-solution.)

The filtrate from the precipitated sulphur contained thiosulphates, sulphites, but no sulphides. Likewise the clear solution, obtained on letting the alkaline solution turbid with sulphur stand, was found to contain no sulphides, only sulphites and thiosulphates appearing to be In this respect we differ from Stingl and Morawski, who present. state, in the equation they give (p. 593), that polysulphides are formed. It would also appear from their equation that in the turbid fluid (from precipitated sulphur) no sulphites are present, which is not true. This we proved by immediate filtration, and testing the clear filtrate for sulphites in the usual way. But we found in this latter case thiosulphates present as well as sulphites, whose joint presence at once indicates the impossibility of tetrathionic acid having been formed, the contrary of which Stingl and Morawski's equation would make apparent. The application of the fact by Stingl and Morawski, that potassium permanganate solution is decolorised without a precipitate and in the cold by the clear filtrate from the precipitated sulphur, to demonstrate the presence of tetrathionic acid in that solution, fails in its object, since the presence of thiosulphates would also account for this deoxidation and decolorisation.

The observations we have made show us that by the action of *aqueous* solutions of the alkaline hydrates a complete rupture of the pentathionic acid molecule may be regarded as taking place, free sulphur, sulphites, and thiosulphates being formed. We were thus led to the adoption of the following equation as illustrating the reaction most probably taking place:—

$2(S_5O_6H_2) + 10NaOH = 3S + 3(Na_2SO_3) + 2(Na_2S_2O_3).$

We at first thought that on re-solution of the sulphur after standing the following reaction occurs, $3S + 3(Na_2SO_3) = 3Na_2S_2O_3$, in which case no sulphites should remain. But sulphites do exist in the cleared solution: hence, as Stingl and Morawski remark, the sulphur is in all probability partly taken up to form sulphide by the excess of caustic soda, and almost simultaneously the sulphide takes up oxygen together with more sulphur, forming thiosulphates. Of the presence of sulphites we have had ample proof. We are perfectly aware of the fact that the reaction we have used for detecting thiosulphuric acid, viz., the action of dilute hydrochloric acid, causing simultaneous precipitation of sulphur and evolution of SO₂, applies equally to the detection of trithionic acid, but it would be very difficult to under-

stand how trithionic acid could be formed under these circumstances, *i.e.*, simultaneously with sulphurous acid. A glance at the structural formula of pentathionic acid, which must belong to this acid (its existence being taken for granted), and the structural formula for its homologue, tetrathionic acid, being known to be—



will now show that our equation would appear to be the simplest and the most natural; also only bodies figure in it whose presence we have proved. In the above formula for pentathionic acid such a splitting off of sulphur also as is indicated by the dotted lines perfectly agrees with the meaning of our equation given above, and now it will be apparent too that if sulphites be formed in the reaction together with separation of sulphur, the formation of trithionic acid can hardly be considered possible. However the same formula shows that our view expressed in the equation proposed is most simply in accordance with the facts we observe, that pentathionic acid is split up by the action of caustic alkali into sulphur, thiosulphuric and sulphurous acid residues.

We now endeavoured to ascertain the conditions under which the finely divided precipitate of sulphur is so comparatively quickly redissolved, after precipitating the Wackenroder solution, with excess of sodium hydrate. For this purpose we took three test-tubes, and introduced into each about an equal amount of finely divided sulphur which had been precipitated from dilute yellow ammonium sulphide solution by addition of hydrochloric acid. Sodium hydrate solution was then added in equal volume to each tube, and in the first was placed a little sodium sulphite solution, in the second a little sodium thiosulphate, and in the third a mixture of these two salts. After standing for about two days, we found in the case of the tube containing the sulphite, complete solution had almost taken place. In the case of the thiosulphate, and of the mixture of thiosulphate and sulphite, however, less solution of the sulphur had been effected.

We find also on precipitating a pentathionic acid solution with an alkaline hydrate, if the precipitate of sulphur be large and be further coagulated by shaking, solution then takes place only after a considerably longer time than is required if the solution be diluted previous to decomposition and shaking be avoided, so that no coagulation occurs. The more rapid solution appears then to ensue when the sulphur is in the finest possible state of molecular division. A mere milkiness or opalescence disappears in about the course of an hour.

With regard to Spring's statement, that the so-called pentathionic acid is nothing more than tetrathionic acid, all the reactions of which it gives, there is one point on which we speak with the most complete confidence, viz., that a solution of tetrathionic acid is not decomposed by alkaline hydrates in the slightest, and therefore it is clear that in Wackenroder's solution a different and much less stable thionic acid exists. But Spring goes further, and states that together with tetrathionic acid a small quantity of hyposulphurous acid is formed by Wackenroder's method, and that it is simply the mixture of these two acids which forms that apparently unstable body termed "pentathionic acid."

For the purpose of testing this question, a freshly prepared Wackenroder solution was carefully treated with an indigo solution of the faintest possible blue tinge. The acid solution was in large excess. This faint blue tinge did not disappear even after warming, and hence we conclude that no hyposulphurous acid was present. We next prepared a solution of hyposulphurous acid by the action of zinc-dust on sulphurous acid solution. A quantity of pure tetrathionic acid was also prepared by the action of iodine on barium thiosulphate, and subsequent removal of barium with sulphuric acid. A small quantity of the hyposulphurous acid was mixed with the tetrathionic acid solution. This solution not only readily decolorised indigo, but yielded not the slightest precipitate of sulphur with potassium and sodium hydrates. Even a strong hyposulphite solution does not precipitate sulphur when treated with KOH, &c., for the alkaline hyposulphites are stable and well defined salts. Both pentathionic and tetrathionic acids coincide in being decomposed by an alkaline sulphide or sulphydrate solution, with precipitation of sulphur. This we have often verified, but an alkaline hydrate or carbonate, which combines with the former acid to form saline compounds rapidly decomposing, combines with the latter to form stable salts.

We next repeated Spring's analysis of the potassium tetrathionate, which he obtained by extracting the acid solution obtained by Wackenroder's reaction with ether, subsequently diluting with alcohol, and precipitating with potassium carbonate. Results were obtained precisely agreeing with the calculated numbers for potassium tetrathionate and with Spring's results generally (see p. 593). The potassium salt was as Spring described it, a snow-white crystalline salt, soluble in water without turbidity or residue. It gave all the reactions of tetrathionic acid, and certainly no precipitate of sulphur with sodium hydrate solution. Two determinations of potassium in the salt gave results showing that the salt was a potassium tetra-thionate:----

Pot	tassium per cent.
(I) 0.1475 gram of salt gave 0.085 gram of K_2SO_4 .	
From I	25.86
(II) 0.1170 gram of salt gave 0.068 gram of K_2SO_4 .	
From II	26.07
Mean	25.97
Calculated for $K_2S_4O_6$	25.86
$,, K_2 S_5 O_6 \dots \dots$	23.35

If the Wackenroder solution be shaken with ether, and the ethereal solution after dilution with alcohol be treated with potash, no precipitation of sulphur takes place, and the solution shows characteristic reactions of tetrathionic acid. On adding, however, a few drops of potash to the residual aqueous solution which had been shaken with the ether, an immediate precipitate of sulphur was thrown down.

We at first thought that we had thus discovered in the ether a means of separating tetra- from penta-thionic acid, and that the Wackenroder solution must contain the latter acid mixed with a small proportion of the former, the tetrathionic acid being soluble, but the pentathionic acid insoluble in the ether. The following experiment showed us we were wrong. A quantity of Wackenroder solution was repeatedly shaken with fresh quantities of ether, with the object of gradually freeing it from tetrathionic acid, but this was found utterly impossible, since after between twenty and thirty agitations the ethereal extract gave unabated indications of the presence of tetrathionic (or pentathionic) acid with the silver nitrate reaction and with litmus-paper. We then suspected that it was merely the pentathionic acid which is slightly soluble in ether, which would account of course for a small quantity being continually taken up after each renewed agitation with ether.

The following experiments solved for us this apparent enigma, and demonstrated also the fallacy of Spring's conclusion, that he had obtained the potassium salt of the actual acid existing in, and by means of the treatment with ether or amyl alcohol, extracted from the Wackenroder solution, and remaining quite intact during the process, simply because the salt he obtained dissolved in water without leaving either residue or turbidity of sulphur. A small quantity of the Wackenroder solution was treated in a test-tube with strong alcohol, and thereafter the alcoholic solution, with ether. By this means a clear ether-alcoholic solution of the whole acid solution taken was obtained. On carefully adding a few drops of a pure caustic soda solution upon the surface of the liquid in the tube, an immediate tur-

bidity was produced just in the upper alkaline layer formed for the instant, evidently owing to separation of sulphur. On sinking through and mixing with the sub-natant ether-alcoholic fluid, the precipitate quickly disappeared again. On adding more caustic soda, a further precipitate appeared, soon disappearing on gentle agitation. It thus became clear to us that a separation of very finely divided sulphur *does* take place, on treating an ethereal pentathionic acid solution with alkalis, but without turbidity, because the finely divided sulphur is instantly dissolved by the ether. In the above experiment on adding excess of soda, at length a yellow ethereal layer was formed in the upper part of the solution, consisting of an ethereal solution of the sulphur, separated in an extremely finely divided condition. It would appear, then, that separation and solution of the sulphur became almost simultaneous processes.

From a further experiment it would appear that the sulphur thrown down in an aqueous solution by the action of alkalis, is precipitated in a physically coarser condition than in an ethereal solution. Some of the Wackenroder solution was mixed with a little potash, whereby a precipitate of sulphur was at once formed, excess of ether and alcohol were then added, but the sulphur was not nearly so quickly or easily dissolved as in the former case, in which the precipitation took place in the ether-alcohol solution.

We thus see why Spring obtained a potassium tetrathionate salt quite free from sulphur, in the manner he describes, for the sulphur, as soon as liberated from the pentathionic acid, was immediately dissolved and taken up by the ethereal alcohol solution. With regard, however, to a tetrathionate being formed in an ethereal or alcoholicethereal solution, and mixed sulphites and thiosulphates in an aqueous solution, we are brought to the conclusion that in the former case a feebler reaction ensues, and less sulphur is abstracted than in the latter case, where more sulphur being set free, a complete disruption of the pentathionic acid molecule takes place, the two cases being thus exemplified:—



No. 1. Action of alkalis in ethereal or ether-alcohol solution.

No. 2. Action of alkalis in aqueous solution on the pentathionic acid molecule.

Synthesis of Tetrathionic and Pentathionic Acids from the same materials.

It now became evident to us that in order to throw clearer light upon the question of the absolute identity of this pentathionic acid, it would be necessary to attempt its synthesis, developing the acid according to a preconceived theoretical scheme, and if by the use in duly modified proportions of the same ingredients its tetrathionic homologue could be formed, of whose identity and constitution little doubt can exist, then it would appear that our grounds of argument as to both identity and constitution of pentathionic acid must be good.

The following theoretical scheme was now drawn up by one of us (W.S.) as a possible means of satisfying the above-named requirements. It was proposed to endeavour firstly to synthesise tetrathionic acid by the action of a solution of iodine in hydriodic acid or potassium iodide, upon lead thiosulphate suspended in water, according to the following equation :—

1)
$$\operatorname{SO_2-O}$$
 H
 $\operatorname{S--Pb}$ I I
 $\operatorname{S--Pb}$ I I
 $\operatorname{S--Pb}$ I I
 $\operatorname{SO_2-O}$ H
 $\operatorname{SO_2-O}$ H
 $\operatorname{SO_2-O}$ H
 $\operatorname{SO_2-O}$ H
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And thereafter, to use a solution of iodine in hydriodic acid, as concentrated as possible, containing about the following proportions :— $2(\text{HI}): 2(I_2).$



This SO₃ as SO₄H₂ would react on the excess of PbS₂O₃, thus :---

 $[PbS_2O_3 + SO_3 = PbSO_4 + SO_2 + S],$ or $3(PbS_2O_3) + 2(HI) + 2(I_2) = H_2S_5O_6 + 3(PbI_2) + SO_3.$ Of course it would be quite possible, as may be anticipated, and as

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we experimentally found, to prepare a lead tetrathionate by the action of a solution of iodine in spirits of wine, on lead thiosulphate, the reaction being the following :—



On treatment with dilute sulphuric acid or sulphuretted hydrogen, the free acid was obtained. I may just remark that the new method, of which the scheme has been just described, for obtaining and preparing pentathionic acid, is the most convenient and expeditious one in existence, for here the difficulty of dealing with finely divided sulphur, refusing to separate on the filter without the introduction of some foreign substance into the solution, is quite overcome.

I. Preparation of Tetrathionic Acid.-Freshly prepared and washed lead thiosulphate, in the state of a thick mud, is mixed with some water, and shaken in a flask with solution of ioline in hydriodic acid, the solution being by no means a concentrated one, and the iodine solution being added little by little, with a thorough agitation after each addition, and finally stopping short of a final decomposition of the whole of the lead thiosulphate. After filtering, any lead in solution is removed by H₂S water, care being taken not to add too much. Sulphuric acid, with subsequent use of barium carbonate to remove its slight excess, is better. By this method, we found it often difficult to avoid the simultaneous formation of varying small quantities of pentathionic acid, whose presence we detected by the slight opalescence produced with caustic alkaline solutions, the well developed reaction with silver nitrate, &c. (vide Table, p. 608), showing that considerable quantities of tetrathionic acid were present. The most convenient method consists in using a potassium iodide solution of iodine, instead of the hydriodic acid solution. A concentrated solution may then be employed. with gentle warming to hasten the reaction. The final product is a pure and clear solution of potassium tetrathionate. Not a trace of pentathionic acid is formed.

II. Preparation of Pentathionic Acid.—Instead of the not very strong solution of iodine in hydriodic acid, a solution so concentrated should now be adopted that iodine is no longer taken up by it, but a residue thereof remains, and to the lead thiosulphate in the state of a thick mud, enough water is added to form with it a thin pasty mass. The

iodine solution is now added gradually with shaking, till on standing for a minute after a fresh addition and agitation, a faintly browncoloured supernatant solution is observed. More water is now added, and the contents of the flask are then heated till the brown colour disappears, when fresh iodine solution is added, till at length a permanent excess remains, even on warming. Lead thiosulphate is now added in very small quantities, with agitation and warming, till the vellow tint of the supernatant fluid disappears, and a colourless solution remains, in which spangles of lead iodide are floating. The mixture after cooling, is now filtered, and hydrogen sulphide is freely passed through the filtrate to separate lead; as soon as this is effected, and the solution, after shaking, smells of H₂S, quite a concentrated and clear solution of pentathionic acid is obtained on again filtering. This solution, however, soon becomes turbid again, probably from contact with slight excess of H_2S left in the fluid. The latter is now removed by a stream of CO₂, or air, and on filtering, evaporation, and again filtering, a concentrated solution is obtained, which should be allowed to stand one day or overnight, when a final filtration is generally needed. The clear liquid now obtained exhibits all the properties of a concentrated solution of pentathionic acid. The method has the several advantages of yielding a purer product than the others, and of doing so with great expedition, and little trouble. The great difficulty of Wackenroder's method, viz., the filtration from finely divided sulphur, is also avoided, for the solution in the case of our method leaves its finely divided sulphur behind with the lead sulphide, with the greatest ease. Dilute sulphuric acid may be used, with perhaps even more convenience for separating the lead than H₂S, the excess being afterwards removed by the addition of just enough BaCO₃, followed by immediate filtration.

Analysis by Kessler's Method.

10 c.c. of the solution of the pentathionic acid prepared by the new method, were now treated with an excess of mercuric cyanide solution, till the precipitate, which was yellow, became quite black. The precipitate was thrown on to a weighed filter, washed, and dried at 100° , till the weight was constant.

HgS + sulphur = 0.2062 gram.

The mixture was then dissolved in strong nitric acid, with addition of KClO₃. After evaporating nearly to dryness, adding HCl, and again evaporating, the sulphuric acid in the diluted solution was determined as $BaSO_4$.

Weight of BaSO₄ due to free sulphur and HgS = 0.4875 gram. This is equivalent to sulphur = 0.0669 , Hence weight of Hg (0.2062-0.0669)..... = 0.1383 , Equivalent to HgS = 0.1615 , And therefore free S = (0.2062-0.1615) = 0.0447 ,

The filtrate from the HgS and free sulphur contained sulphuric acid, which was estimated. BaSO₄ due to sulphuric acid, = 0.3330 gram.

The relative weights of HgS, free \tilde{S} , and H₂SO₄ are then as follows:—

$$HgS = 0.1615$$
; $S = 0.0447$; $H_2SO_4 = 0.1400$;

Dividing these numbers by their equivalent weights, the following numbers were obtained :---

HgS. 0.1615÷ 2320.0007 or 1. = = S.... 0.0447÷ 32= 0.0014 or 2. = H_2SO_4 0.140098 0.0014 or 2. = ÷ = HgS. S. H₂SO₄.

These ratios 1:2:2 exactly coincide with Kessler's equation, $H_2S_5O_6 + Hg(CN)_2 + 2H_2O = HgS + S_2 + 2H_2SO_4 + 2HCN.$ 1:2:2:2

With a fresh pentathionic acid solution not so carefully prepared and probably containing some tetrathionic acid, the following numbers were obtained :—

HgS.	_	0.2068	÷	232	=	0.00089:1
S	=	0.0466	÷	32	=	0.00146 : 1.64
H_2SO_4	=	0.1739	÷	98	=	0.00177:2

We have reason to believe that under given conditions the pentathionates can also be prepared, and we hope before long to lay the results of our experiments in this direction before the Society. The following table of the most characteristic reactions of the thionic acids may prove useful :--

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Reactions to distinguish Tetra- and Penta-thionic Acids from each other, and from the other Thionic Acids.

Reagents.	Dithionic acid, H ₂ S ₂ O ₆ .	Trithionic acid, $H_2^2S_3O_6$.	Tetrathionic acid, H ₂ S ₄ O ₆ .	Pentathionic acid, H ₂ S ₅ O ₆ .	$\mathbf{T}_{\mathbf{z}}$
Jaustic potash	No precipitate	No precipitate	No precipitate	Immediate precipitate of sul- phur, redissolving gradually on standing, if not in much	AKAMAT
Dilute hydrochloric	No action	Evolution of SO ₂ , and pre-	No action	excess and coagulated. No action.	SU A
Mercurous nitrate	No precipitate	Immediate black precipi- tate, becoming white on	Yellow precipitate, gradually darkening.	At first yellow precipitate, turning white with excess of	ND S
illver nitrate	No precipitate	standing. Yellow precipitaté, soon becoming black.	Yellow precipitate, soon turn- ing black, and also on adding	reagent on standing. Yellow precipitate, gradually darkening ; black on adding	SMITH
Ammoniacal silver ni- trate.	I	No brown coloration, even on standing. On warm-	No dark or brown coloration, even on standing, unless	Almost immediate brown colora- tion, becoming black on warm-	ON F
Mercuric cyanide	No precipitate	ing, Ag2S formed.	warmed. At first yellow precipitate; turns black on warming,	Ing. At first yellow precipitate, gra- dually turning black on heat-	PENTA
Mercuric chloride	No precipitate	Yellow precipitate, be- coming white with ex-	with evolution of HUN. On warming, white precipitate.	mg, with evolution of HUN. On warming, whitish yellow precipitate.	THION
Potassium sulph-hy-	1	cess of reagent.	White precipitate of sulphur.	White precipitate of sulphur.	IC A
Dilute solution of potassium perman- ganate.	One drop, immediate brown precipitate.	One drop, immediate brown precipitate, even in presence of dilute SO, H.	Decolorised, without addition of dilute H ₂ SO ₄ .	Decolorised, without addition of dilute H_SO4.	CID.
		0.04112.			

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