XXVI.—On Pentathionic Acid. (Part II.)

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SINCE the publication of Part I of the above research (see *Chem. Soc. J.*, 1880, Trans., 594, and *Annalen*, **207**, 68), a considerable amount of work has been done and published, all of which has gone in confirmation of the conclusion arrived at as the result of our research. The conclusion was in the affirmative as regards the existence of pentathionic acid. The writings of the authors of the subsequent work above referred to, evince some misunderstanding of our methods and results in certain particulars, and this we desire to correct.

The first author, Mr. V. Lewes (*Chem. Soc. J.*, 1881, Trans., 68), proceeds at the outset of his paper to condemn any methods of proof of the existence of pentathionic acid based on analyses of the Wackenroder solution, because, he says, an acid to which he gives the formula $\text{H}_2\text{S}_6\text{O}_6$ may be present, together with tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$, exactly molecule for molecule of each of these acids. Be it remembered, however, that at the time of writing this paper, Mr. Lewes had never isolated any such acid as $\text{H}_2\text{S}_6\text{O}_6$, neither has anyone else since, much less has its existence been proved in the Wackenroder solution. Mr. Lewes' objection to our use of sulphuretted hydrogen in removing the small quantities of lead existing as lead iodide in the acid solution which we obtained in our synthetic formation of pentathionic acid, on the ground of Kessler's observation that lead tetrathionate, if present will, when decomposed by H_2S in presence of PbS , yield SO_2 , which, with H_2S , will produce pentathionic acid, would be plausible had he not overlooked the fact that on page 15, *Chem. Soc. J.*, *loc. cit.*, we mention the greater convenience which we found to follow the use of dilute sulphuric acid, in as small excess as possible, to remove lead, followed by the use of a little barium carbonate, and immediate filtration.

Spring has advanced the objection that our synthesis of pentathionic acid is only a virtual repetition of Wackenroder's method, since the action of iodine dissolved in hydriodic acid would be to set free SO_2 and H_2S , which would then react in the known manner. This we cannot allow, for in our process neither is H_2S set free, nor is S precipitated as in the Wackenroder preparation; in fact all the phenomena observed in our method point to the fact that nascent groups are split off, immediately thereafter to re-unite in a different arrangement, with considerable smoothness, which is not the case in Wackenroder's

method. Here a bulky precipitation of sulphur ensues. Hence we consider that our structural equation, given on page 13 (*Chem. Soc. J.*, August, 1880), faithfully indicates the meaning of the process.

Th. Curtius (*J. pr. Chem.* [2], **24**, 225) re-investigates what he believes we intended as a complete inquiry into the precise action of the alkalis and alkaline earths upon a pentathionic acid solution. The above, however, was not our object. On this subject we commence by quoting (this Journal, 1880, Trans., 7) Stingl and Morawski's experiments and results as regards the precipitation of sulphur, more especially as *a characteristic test for pentathionic acid*. We further used magnesia as a reagent for the above purpose, preferring it to the other alkaline earths, because soluble decomposition-products would result from its use in excess (sulphites and thiosulphates) in the course of the experiment. The sulphur precipitated during the experiment would then ultimately be obtained as a pure sulphur, and not mixed with insoluble salts, as would have been the case had the other alkaline earths been employed. The success of this experiment demonstrated Spring's error, when, using barium carbonate, he obtained ultimately a precipitate which he said consisted of insoluble or sparingly soluble salts and a mere trace of sulphur, insinuating that the apparent production of precipitates of sulphur under such circumstances, had misled former observers, for these precipitates chiefly consisted of sparingly soluble salts, the sulphur accompanying them being quite insignificant in amount. This was used, together with the fact that he obtained a barium tetrathionate by the above treatment, to endeavour to prove that the Wackenroder solution contained not pentathionic acid, but only tetrathionic acid. Thus our motive in using magnesia, with which we obtained a considerable precipitation of sulphur, is explained, this motive having been misunderstood both by Curtius and by Spring.

Th. Curtius states that "Smith and Takamatsu consider the possibility of the formation of tetrathionates as excluded, in the decomposition of the pentathionic acid molecule with carbonates and hydrates of the alkalis and alkaline earths, only holding as possible that sulphites and thiosulphates are formed."

We do no such thing, however; some of the earliest results we obtained in our research showing us clearly that tetrathionates *are* formed, with precipitation of sulphur, on treating pentathionic acid solutions with barium carbonate. Not considering at that time that these results had any special bearing upon our principal theme, we held them over for future work. We were also perfectly aware that by partial saturation with dilute alkalis tetrathionates are formed. (See page 12, *Chem. Soc. J.*, August, 1880.)

Effect of Neutralising with Barium Carbonate a Solution of Pentathionic Acid in Dilute Alcohol.

We now proceed to give the results referred to, proving that the action of pentathionic acid upon barium carbonate, used to neutralise it, results in the formation of barium tetrathionate and free sulphur.

A weak alcoholic solution of pentathionic acid had been neutralised with freshly precipitated barium carbonate and filtered. The clear solution was then left for a long time in a dry atmosphere. A crystalline salt was thus obtained, which was collected, drained, dried, and analysed with the following results:—

Weight of salt taken	0.5570 gram.
Weight of BaSO ₄ after ignition with a drop of H ₂ SO ₄	0.3279 „

This corresponds to 34.61 per cent. Ba.

Weight of salt taken	0.4200 gram.
Weight of BaSO ₄ obtained on oxidation with HNO ₃ and KClO ₃ and precipitation with BaCl ₂ solution	0.9884 „

This corresponds to 32.33 per cent. S.

	Calculated for BaS ₄ O ₆ + H ₂ O.	Found.
Barium	34.51	34.61
Sulphur	32.24	32.33

Further, a freshly prepared quantity of pentathionic acid was mixed with a large amount of ordinary methylated alcohol. The clear solution was then neutralised with BaCO₃ and filtered. The precipitate was almost insoluble in water. It was repeatedly boiled with fresh water, the filtrates being collected. On cooling they deposited a white crystalline precipitate, which, when collected, dried over sulphuric acid, and analysed, gave the following numbers:—

Weight of salt taken	0.1485 gram.
BaSO ₄ obtained by igniting with drop of SO ₄ H ₂	0.0885 „

This corresponds to 35.04 per cent. Ba.

Weight of salt taken	0.3545 gram.
BaSO ₄ obtained on oxidising with HNO ₃ and KClO ₃ and precipitation with BaCl ₂	0.8259 „

This corresponds to 32.03 per cent. S.

	Calculated for $\text{BaS}_4\text{O}_6 + \text{H}_2\text{O}$.	Found.
Barium.	34.51 per cent.	35.04 per cent.
Sulphur	32.24 „	32.03 „

These results were obtained when at the outset we endeavoured to obtain a barium salt of pentathionic acid. We thus proved to our own satisfaction that the attempt to neutralise pentathionic acid with alkaline earth carbonates simply results in the formation of tetrathionates, with separation of sulphur.

Effect of Excess or otherwise of Solutions of Alkalis on Pentathionic Acid Solutions.

With respect to the action of alkaline solutions, we simply referred in our paper to the action of aqueous solutions of the alkaline hydrates added *in excess*, in producing an immediate copious precipitate of sulphur (which reaction does not take place in solutions of tetrathionic acid), and hence furnishing a valuable and sharply defined line of distinction between penta- and tetra-thionic acids.

The equation we gave, $2\text{S}_5\text{O}_6\text{H}_2 + 10\text{NaOH} = 3\text{S} + 3\text{Na}_2\text{SO}_3 + 2\text{Na}_2\text{S}_2\text{O}_3$, was intended to illustrate the reaction taking place, and to this we must firmly adhere, nothing to the contrary having been proved; and it is also certain that the products of the reaction are those given in our equation.

With regard to the accuracy of the equation given by Stingl and Morawski, $5\text{H}_2\text{S}_5\text{O}_6 + 10\text{HKO} = 5\text{K}_2\text{S}_4\text{O}_6 + 5\text{S} + 10\text{H}_2\text{O}$, we perfectly agree to its authority where the pentathionic acid solution is treated with an amount of dilute alkali, so as to fall far short of saturation. But we seriously dispute this authority in cases where alkalis in excess are used. In this latter case Stingl and Morawski give an equation, representing the second stage of the decomposition, as $5\text{K}_2\text{S}_4\text{O}_6 + 5\text{S} + 18\text{KOH} = 7\text{K}_2\text{S}_2\text{O}_3 + 6\text{K}_2\text{SO}_3 + \text{K}_2\text{S}_5 + 9\text{H}_2\text{O}$, and this equation we entirely dispute.

In order to put the question of the correctness of the equation of Stingl and Morawski, and our own, to a thorough re-examination, a quantity of the pentathionic acid (Wackenroder's solution) was prepared by Mr. W. H. Green, to whom we are indebted for the careful way in which he has conducted these latter special experiments for us. The strength of the acid obtained ultimately by concentration, was now determined by oxidising a known volume of it with hydrochloric acid and potassium chlorate, with subsequent precipitation with barium chloride. From this it was found that 10 c.c. of the pentathionic acid solution contained 0.668 gram sulphur = 1.077 gram $\text{H}_2\text{S}_5\text{O}_6$.

Now, pure potassium hydrate and pentathionic acid solutions were

taken in such weights as exactly to realise the proportions stated in Stingl and Morawski's equation, $5\text{H}_2\text{S}_5\text{O}_6 + 10\text{KOH} = 5\text{K}_2\text{S}_4\text{O}_6 + 5\text{S} + 10\text{H}_2\text{O}$; that is to say, 1.045 gram caustic potash and 22.3 c.c. (= 2.403 grams $\text{H}_2\text{S}_5\text{O}_6$) pentathionic acid solution, were taken. The potash was dissolved in water to form a dilute solution, which was then added to the pentathionic acid solution. A precipitate of sulphur was obtained, but by no means a copious one. On filtering a portion and testing the filtrate, *only tetrathionates* could be discovered, no thiosulphates or sulphites whatever.

On adding a further quantity of potash, so that it may be in excess, a very abundant additional precipitation of sulphur took place, and, on filtering and examining the filtrate, only sulphites and thiosulphates were discovered, but no tetrathionates. Neither in this filtrate nor in the former one were sulphides detected: hence Stingl and Morawski err in this respect. But we have already stated that potash does not decompose tetrathionic acid, and does not yield a precipitate of sulphur with it. If this be so, the question will be asked, how is it that in the further and final treatment with potash, tetrathionates are undoubtedly decomposed, only mixed sulphites and thiosulphates remaining? The solution of this problem rests on the fact that tetrathionic acid, though stable in presence of alkalis, is at once decomposed by alkaline sulphides—

(see Roscoe and Schorlemmer's Treatise, vol. i, p. 353).

Hence we conclude that on partial saturation of a pentathionic acid solution with an alkali, say potash, we may get a certain amount of potassium pentathionate formed, together with the realisation of Stingl and Morawski's equation, $5\text{H}_2\text{S}_5\text{O}_6 + 10\text{KOH} = 5\text{K}_2\text{S}_4\text{O}_6 + 5\text{S} + 10\text{H}_2\text{O}$. This accords with V. Lewes' experience (*Chem. Soc. J.*, 1881, Trans., 71, 74, &c.). If now the opalescent solution obtained on filtering be treated with more potash, then the 5S in the above equation previously insoluble and inert (no free alkaline hydrate being present to dissolve it) is partially dissolved to form alkaline sulphides, when at once $\text{K}_2\text{S}_4\text{O}_6 + \text{K}_2\text{S} = 2\text{K}_2\text{S}_2\text{O}_3 + \text{S}$ follows, and also our equation as regards pentathionates still left behind in the fluid: $2\text{K}_2\text{S}_5\text{O}_6 + 8\text{KOH} = 3\text{S} + 3\text{K}_2\text{SO}_3 + 2\text{K}_2\text{S}_2\text{O}_3$. This fully explains the further copious precipitation of sulphur ensuing on further addition of alkaline hydrates. We cannot admit Curtius' view that with employment of excess of alkaline hydrate there is still an intermediate formation of alkaline tetrathionate: for the existence of tetrathionates is barely possible where sulphur and alkaline hydrate occur together, and quite impossible where the sulphur is in the nascent state. Doubtless, then, where the alkali is in excess, 2 atoms

of sulphur are at once split off the pentathionic acid molecule, yielding directly the groups $\text{K.SO}_2\text{OK}$ and $\text{KS.SO}_2\text{OK}$.

On page 12 (*Chem. Soc. J.*, 1880, Trans.) we show that when the pentathionic acid solution is shaken with ether, and the ethereal solution treated with alcohol, the whole being then treated with a little potash solution, *tetrathionate* is obtained as the decomposition-product. The action is feeble because the points of contact are diminished, as it were, through the diminished solubility of the potash in the new menstruum. Now Lewes has shown that by far undersaturating the Wackenroder solution with very dilute alkali, tetrathionates are formed, besides pentathionates, and can be crystallised out; and this agrees with a more recent observation of the action of a weak ether-alcohol solution of alkaline hydrate on pentathionic acid: for by working on a larger scale, we have succeeded, by the gradual evaporation of such a solution, in obtaining mixed crops of crystals consisting of both pentathionates and tetrathionates.