XLVIII.—*On the Preparation of the Pentathionates.*

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IN a paper published in *Liebig's Annalen*, Bd. **213** [3], 329—363, Professor Spring denies that any results so far obtained possess sufficient authority to be accepted as proof of the existence of pentathionic acid, either in the free state or combined to form pentathionates. He combats the statement of V. Lewes, detailed in this Journal (**39**, 68), that he had prepared and analysed the potassium and barium salts of the acid in question, by relating his own lack of success in the attempted repetition of Lewes's preparations and analyses. Spring states that in attempting to prepare the potassium and barium pentathionates, in one case he obtained an impure salt containing more sulphur than a tetrathionate but less than a pentathionate, and in the other, crystals containing free sulphur, and dissolving in water to a turbid and acid liquid. He finally states it as his opinion that the so-called pentathionic acid consists of a solution of sulphur in tetrathionic acid, and that salts obtained from this acid are simply tetrathionates containing admixed sulphur.

The following experiments were undertaken, in accordance with Professor Roscoe's wish, for the purpose of testing the accuracy of Lewes' results. The first step taken was that of writing to Mr. Lewes, to invite him to send the exact description of the way in which he had operated in obtaining his preparations, and to this he cordially responded.

Sulphuretted hydrogen and sulphur dioxide gases were simultaneously passed into 3 litres of distilled water contained in a Winchester quart bottle, for about 32 hours, the sulphur dioxide being kept slightly in excess.

A normal caustic potash solution was prepared, and the Wackenroder solution obtained as above, without separating its suspended sulphur, was titrated with it. 10 c.c. of Wackenroder solution required 5 c.c. of normal potash solution for complete neutralisation, or 2.5 c.c. for half neutralisation. To 3000 c.c. of Wackenroder solution, 750 c.c. normal potash solution were added, slowly, and with continual stirring. After standing some time, the solution was filtered, the filtrate passing through perfectly clear. This clear filtrate smelt strongly of sulphur dioxide, and a portion treated with excess of potash failed to give any precipitate of sulphur, possibly because the sulphur at once passes into combination with the sulphurous acid existing in the liquid, and in presence of the alkali forms thiosulphate. The filtered solution was now evaporated on the water-bath, when sulphur was deposited and sulphur dioxide evolved, and on treating a portion with potash, an abundant precipitate of sulphur was obtained.

After concentrating on the water-bath, the liquid was placed in a partial vacuum over sulphuric acid, when in about eight days a crop of perfectly clear and transparent crystals was obtained, which on analysis proved to be anhydrous potassium tetrathionate.

	Salt taken. Gram.	K_2SO_4 . Gram.	Percentage of potassium.		Calculated for $K_2S_4O_6$.
I.	0.768	gave 0.438	= 25.60	} Mean = 25.76	25.87
II.	0.526	„ 0.303	= 25.93		
			Percentage of $BaSO_4$. sulphur.		
	0.584	„ 1.7857	= 42.0		42.35

On further standing, more tetrathionate crystals were deposited from the mother-liquor, and after some time a third crop was obtained. On examining this crop under the microscope, part of the crystals clearly resembled the previous crops, but amongst them were seen some crystals of quite different form. It was further found that if from this mixed crop a crystal, now recognised by the above analysis to be the tetrathionate, was carefully picked out, dried in a small piece of

filter-paper, placed in a watch-glass, dissolved in a little water, and then treated with a drop of caustic soda solution, not the slightest change appeared. The same process repeated in another watch-glass with a crystal of the different form, resulted in the immediate appearance of a white precipitate of sulphur.

Since all the crystals in this crop were perfectly transparent, and yielded perfectly clear and neutral solutions, there can be no question, simple though the method may be, that the former, being crystals of potassium tetrathionate, the latter must be those of a totally different and less stable substance, decomposed by alkali.

This mixed crop of crystals was analysed, and gave the following numbers:—

	Salt taken.	K_2SO_4 .	Per cent. of K.	
I.	0.455	gave 0.2315	= 22.96	} Mean = 22.91
II.	0.3375	„ 0.172	= 22.87	
			Per cent. of	
		$BaSO_4$.	sulphur.	
I.	0.287	„ 0.9082	= 43.45	
		or K : S :: 2 : 4.6		

After some time, two other crops of mixed crystals were obtained, and these still showed on analysis the relation K : S :: 2 : 4.6.

Fourth Crop.

	Salt taken.	K_2SO_4 .	Per cent. of K.	
I.	0.283	gave 0.153	= 24.2	} Mean = 24.07 per
II.	0.268	„ 0.143	= 23.95	
			cent. of potassium.	
			Per cent. of	
		$BaSO_4$.	sulphur.	
I.	0.245	„ 0.802	= 44.93	
		or K : S :: 2 : 4.6.]		

Fifth Crop.

	Salt taken.	K_2SO_4 .	Per cent. of K.	
I.	0.1515	gave 0.0785	= 23.25	} Mean = 23.24 per
II.	0.1830	„ 0.0970	= 23.23	
			cent. K.	
			$BaSO_4$.	Per cent. of S.
I.	0.152	„ 0.4815	= 43.50	
		or K : S :: 2 : 4.6		

The next crop was composed of larger crystals, and the strange crystals were so abundant in quantity as to be easily discernible, and indeed a quantity was carefully selected and analysed, with the following result:—

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	Salt taken. Gram.		K ₂ SO ₄ .	Percentage of potassium found.		Calculated for K ₂ S ₅ O ₆ + H ₂ O.
I.	0.1595	gave	0.0785	= 22.08	} Mean = 22.063	22.13
II.	0.052	„	0.0255	= 22.057		
	Gram.		BaSO ₄ .	Per cent. of sulphur.		
	0.218	„	0.7217	= 45.45		45.42
	Gram.		H ₂ O.	Per cent. H ₂ O.		
	0.2745	„	0.0205	= 7.4		5.11
			or K : S :: 2 : 5.0			

The water of crystallisation was determined by combustion with lead monoxide, and the difficulty of excluding traces of moisture probably accounts for the difference between the found and calculated percentages of water.

These crystals thus analysed were *colourless* and *transparent*, and also dissolved in water to a perfectly *clear neutral solution*.

The following are the results of the analyses of all the crops obtained, ending with the analysis of the selected crystals of pentathionate :—

1st crop.....	K : S :: 2 : 4.0	
2nd „	K : S :: 2 : 4.0	
3rd „	K : S :: 2 : 4.6	} mixed.
4th „	K : S :: 2 : 4.6	
5th „	K : S :: 2 : 4.6	
6th „	K : S :: 2 : 5.0	selected.

Mr. H. Baker kindly determined the crystalline form of both the tetra- and penta-thionate.

Examined microscopically the crystals of potassium tetrathionate and pentathionate are both seen to belong to the rhombic system, but differ entirely from each other, since the tetrathionate is most markedly hemimorphous, whilst the pentathionate is holohedral.

The general form of the tetrathionate is that of a thick but flat crystal, terminated at one end by a pair of slant faces meeting sharply in a point, at the other by a slant face at right angles to the length of the crystal. The depolarising directions are parallel and at right angles to the length, and in the polariscope one of the two optical axes is just visible.

The principal forms are $P\infty$, P , and $P\infty$ (no measurements having been made, the signs $\sim$ and $-$ are only used for distinction). Two faces of $P\infty$ give the crystals their tabular appearance, and $P\infty$ is the hemimorphous form. The plane of the optical axes is $\infty P\infty$.

The pentathionate forms short thick prisms, four or six-sided, with

flat terminal faces and small subsidiary pyramidal or domal faces. Forms $\infty P . 0 P . \infty P \infty . P \infty$. The depolarising directions are parallel and at right angles to the prism-edges. Other crystals showed more numerous faces, but could not be made out under the microscope.

It was observed, in the course of several attempted preparations of potassium pentathionate from half-neutralised Wackenroder solutions, that on evaporation even in a vacuum over sulphuric acid, sometimes the liquid persistently remained turbid, even after many filtrations, and the crystals obtained in such cases were contaminated with sulphur and quite unfit for analysis, exactly according with Spring's experience in his attempt to repeat Lewes' method of preparation. It is not easy to say in what respect the mode of conducting the preparation when pure specimens were obtained differed from that in which an impure and less stable product was the result.