LXXIII.—*The Action of Potassium Sulphite on Potassium Tetrathionate in Aqueous Solution.*

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I HAVE previously shown (Trans., 1892, **61**, 181, 1083) that iodine does not act on a mixture of a sulphite and thiosulphate in aqueous solution to form a trithionate directly, but oxidises the sulphite to sulphate and converts the thiosulphate into tetrathionate. When, however, the iodine is insufficient in quantity to oxidise all the sulphite to sulphate and convert all the thiosulphate into tetrathionate, Spring (*Bull. Acad. roy. Belg.*, 1874, [ii], **38**, 112) has shown that, in the case of the potassium salts, potassium trithionate is formed. The formation of a trithionate in such circumstances may be due to some of the unoxidised sulphite abstracting sulphur from the tetrathionate in accordance with the equation :

I have endeavoured in the present investigation to ascertain how far this equation represents the truth.

In previous investigations in which a sulphite was either a member of the initial system or a product of the change, I made use of the joint estimation of the total iodine titration-value and of the acidity developed in the solution after such titration was complete in determining how much of the iodine titration-value was represented by the sulphite present, and I have again employed this method.

Preparation of Potassium Trithionate, Tetrathionate, and Pentathionate.

Potassium trithionate was prepared according to the method described by Plessy (*Ann. Chim. Phys.*, 1844, [iii], 11, 182). The salt, twice crystallised from aqueous alcohol, gave on ignition a quantity of potassium sulphate which was 64·30 per cent. of the weight of the trithionate instead of the theoretical 64·44 per cent. The aqueous solution of the salt was quite neutral, gave no precipitate with barium chloride, and occasioned no darkening in an ammoniacal solution of silver nitrate.

Potassium tetrathionate was prepared according to the method described by Kessler (*Pogg. Ann.*, 1848, 74, 249). The salt, twice crystallised from aqueous alcohol, gave on ignition a quantity of potassium sulphate which was 57·66 per cent. of the weight of the tetrathionate instead of 57·61 per cent., the theoretical quantity. The aqueous solution of the salt was neutral, and gave no indication of the presence of sulphate or pentathionate.

Potassium pentathionate: in the preparation of this salt according to the method described by Debus (*Trans.*, 1888, 53, 278), it was found quite possible to distinguish "six-sided prisms with pyramids only at one end" (tetrathionate) from "four-sided rhombic or six-sided star-like plates" (pentathionate).

Preliminary Experiments.

At the outset it was established that, with aqueous solutions of concentrations corresponding with those employed in the course of this research, (a) iodine has no appreciable immediate action on potassium trithionate, tetrathionate, or pentathionate, or on any two or all three of these salts, and (b) potassium sulphite and thiosulphate respectively preserve their iodine titration-values when mixed with potassium trithionate, tetrathionate, or pentathionate, or with any two or all three of these salts, provided that the titration is made within a few minutes of mixing.

With the view of ascertaining whether either potassium sulphite or thiosulphate has any action on potassium trithionate in aqueous solution, four portions of 100 c.c. of boiled distilled water saturated with carbon dioxide were taken. In each of the first three of these, 0·27

gram of potassium trithionate was dissolved, and to the second and third a quantity of potassium sulphite and thiosulphate was respectively added, so that the proportion of sulphite to trithionate was $2\text{K}_2\text{SO}_3 : \text{K}_2\text{S}_3\text{O}_6$, and of thiosulphate to trithionate, $2\text{K}_2\text{S}_2\text{O}_3 : \text{K}_2\text{S}_3\text{O}_6$. The fourth portion contained the same quantity of potassium thiosulphate as the third, but no trithionate. Each flask containing these solutions was fitted with an indiarubber stopper, through which passed two glass tubes, one serving as entrance tube for a continuously passing stream of carbon dioxide, and the second, which served as exit tube, being connected with a second flask similarly fitted and containing 100 c.c. of boiled distilled water saturated with carbon dioxide to which a small quantity of filtered starch solution and a drop of the iodine titrating solution were added.

The determination after the lapse of twenty-four hours of the iodine titration-values showed that the thiosulphate and trithionate had reacted to an extent just appreciable, but that the sulphite and trithionate had not reacted at all. The experiment also established that neither the trithionate nor the thiosulphate solution had undergone any change within the twenty-four hours. After seventy-two hours, the reaction between the thiosulphate and trithionate had progressed further, and represented, after making an allowance for the almost negligible decomposition of the trithionate solution in this period of time, a conversion of about 4 per cent. of the thiosulphate present into sulphite.

An exactly similar experiment was carried out with the view of ascertaining whether, if tetrathionate and thiosulphate are present together in aqueous solution in the proportion $\text{K}_2\text{S}_4\text{O}_6 : 2\text{K}_2\text{S}_2\text{O}_3$, any formation of sulphite could be detected. Even after seventy-two hours, no alteration in the iodine titration-value of such mixed solution, and no decomposition of the control solutions of tetrathionate and thiosulphate respectively, could be detected.

In ascertaining by means of the iodine titration, in conjunction with the developed acidity determination, the nature and extent of the change which the sulphite undergoes, it must be noticed that in no case is the iodine titration more than a record of the quantity of converted and unconverted sulphite in the solution at any particular moment; it is not a record of the total change the sulphite may have undergone. Further, before we should be justified in deducing from a knowledge of the nature and extent of the change the sulphite has undergone, the nature and extent of the change the tetrathionate has undergone, we must ascertain whether any, and, if so, what, secondary changes are possible and whether they actually occur. If potassium sulphite and tetrathionate react in aqueous solution, the changes which should be possible would seem to be: (a) the

direct change, $K_2SO_3 + K_2S_4O_6 = K_2S_2O_3 + K_2S_3O_6$; (b) re-formation of the original system if the change is reversible; (c) reaction between unchanged tetrathionate and potassium thiosulphate, which change may also be reversible, $K_2S_4O_6 + K_2S_2O_3 = K_2S_5O_6 + K_2SO_3$.

The determination of the iodine titration-value with the view of estimating the extent of the conversion of sulphite into thiosulphate would give no indication of this secondary change of tetrathionate into pentathionate, supposing it to occur; but such secondary change is at the expense of tetrathionate, and consequently we must ascertain whether it occurs, and to what extent, before we can deduce the nature and extent of the change the tetrathionate undergoes from a knowledge of the nature and extent of the change the sulphite suffers.

With the view of ascertaining whether this formation of pentathionate actually occurs when potassium sulphite and tetrathionate react in aqueous solution, and, if so, to what extent, the reaction of potassium pentathionate with an ammoniacal solution of silver nitrate was examined in the hope that it might possibly form an approximate quantitative method of estimating pentathionates.

The ammoniacal solution of silver nitrate was prepared by dissolving 2 grams of the crystallised salt and 50 c.c. of concentrated aqueous ammonia solution in 200 c.c. of water. The strongest solution of potassium pentathionate contained 0.361 gram dissolved in 100 c.c. Into a number of test-tubes of approximately the same diameter, portions of 10 c.c. each of the ammoniacal silver nitrate solution and an equal volume of the solution of pentathionate were run. The times were recorded which elapsed before coloration was first detectable, and, in the case of stronger solutions of pentathionate, the times were also recorded which elapsed before the coloration equalled that of an unchangeable standard. In this manner, the effect of (a) diminishing the concentration of the pentathionate solution, and (b) the presence of other substances in solution, was investigated.

(a) The effect of diminishing the concentration of the pentathionate solution is shown from the tabular statement on p. 802 of the results obtained.

(b) The effect of the presence of other substances in solution was investigated with the following results.

Using a solution of pentathionate twenty times as dilute as the strongest used in determining the effect of dilution, potassium thiosulphate, trithionate, or tetrathionate, when present in equimolecular quantities relatively to the pentathionate, did not diminish the rapidity with which the darkening with ammoniacal silver nitrate occurred in their absence. Potassium sulphite, on the other hand, not only diminished the rapidity, but also the extent of coloration. Using the twenty times diluted pentathionate solution, potassium sulphite

	First coloration detected.	Coloration equalled standard.
The strongest solution of pentathionate (0.361 gram in 100 c.c.)	Immediately.	After 10 minutes.
The strongest solution diluted 10 times ...	"	" 25 "
" " " 20 " ...	Within half a minute	Coloration never equalled that of standard.
" " " 100 " ...	Within five minutes	
" " " 1000 " ...	Not within first hour (After 24 hours, trace of darkening detected)	

when present in quantities twice the equivalent, the equivalent, and $1/5$ th the equivalent proportion of the pentathionate present, retarded the first appearance of colour thirty minutes, twenty minutes, and a fraction of a minute respectively. Even after twenty-four hours the coloration in the two first cases was still extremely faint, and in the third case was unquestionably less intense than in the experiment where no sulphite had been present. It was further found that the addition of potassium sulphite to a solution of ammoniacal silver nitrate and pentathionate, in which the darkening was proceeding, arrested the same. With the exception of the latter experiment, in every case the method of performing the test was to run into the test-tubes the ammoniacal silver nitrate solution, then the solution of the substance the effect of which was to be determined, and, lastly, the pentathionate solution.

The experimental investigation of the reaction of potassium thiosulphate with potassium trithionate and tetrathionate was repeated, and the ammoniacal silver nitrate test applied to the product of such reaction. The flasks previously used were again employed, and contained (1) a solution of potassium tetrathionate and thiosulphate; (2) a solution of potassium trithionate and thiosulphate; (3) a solution of potassium tetrathionate and thiosulphate, and (4) a solution of potassium trithionate and thiosulphate. The quantity of the thiosulphate was twice the equimolecular proportion of the trithionate or tetrathionate present. The solutions contained in (1) and (2) were made with boiled water saturated with carbon dioxide, and those in (3) and (4) with ordinary distilled water. Through (1) and (2) a stream of carbon dioxide passed continuously, and through (3) and (4) a current of air was drawn for the first and last two of the twenty-four hours.

The determination of the iodine titration-value at the end of twenty-

four hours of portions of 10 c.c. of the contents of the four flasks showed :

(a) In (1) and (3) the thiosulphate remained unchanged.

(b) In (2) some 3 per cent. of the thiosulphate had become converted into sulphite, and the sulphite remained as such in the solution.

(c) In (4) some of the thiosulphate had become converted into sulphite, and the sulphite had been partly oxidised.

The application of the ammoniacal silver nitrate test to portions of 10 c.c. of the contents of the four flasks showed : (a) in (1) and (3) an immediate and considerable pentathionate indication, (b) in (2) and (4) an extremely faint indication of pentathionate.

Hence, from these results, potassium tetrathionate and thiosulphate do react in aqueous solution to form pentathionate and sulphite, but the latter substance immediately reacts with excess of tetrathionate to form trithionate and regenerate thiosulphate. Whether the whole of the tetrathionate thus becomes converted into pentathionate and trithionate, or whether the change between thiosulphate and tetrathionate is a reversible one, the above experiment does not provide one with the means of deciding. Certainly the ammoniacal silver nitrate test points to a considerable transformation into pentathionate.

The rapid diminution in the iodine titration-value of a mixed solution of potassium sulphite and pentathionate shows that these two salts quickly react in aqueous solution. When potassium sulphite reacts in equivalent proportions with pentathionate in aqueous solution, the solution containing 0.361 gram of the pentathionate in 100 c.c., the diminution in the iodine titration-value of the solution at the end of fifteen, thirty, forty-five, and sixty minutes after mixing equalled 43.4, 46.3, 47.1, and 47.3 per cent. respectively of the initial iodine titration-value.

If the sulphite abstracts sulphur from the pentathionate and thereby becomes converted into thiosulphate, the diminution in the iodine titration-value if the reaction completed itself would equal 50 per cent. The above values clearly point to the attainment of a limit somewhere in the neighbourhood of a 50 per cent. diminution, and from them it may be inferred that the general nature of the reaction between potassium pentathionate and sulphite is that the sulphite abstracts sulphur from the pentathionate and itself becomes converted into thiosulphate. Debus has suggested that the sulphite when reacting with the pentathionate decomposes into

(Trans., 1888, 53, 333), and that the change proceeds according to the equation :

If the reaction proceeded in accordance with this equation and completed itself, the iodine titration-value, supposing no sulphur dioxide to escape, would, instead of diminishing, be increased by 83.3 per cent. Supposing the pentathionate and sulphite to have been originally present in equimolecular proportions, and supposing the excess of pentathionate to react with sulphurous acid according to the equation:

the increase in the iodine titration-value, if the latter reaction completed itself, would be 50 per cent. The fact that in place of an increase in the iodine titration-value we have a diminution approximating to 50 per cent. shows that the general nature of the reaction is not that indicated by the former of the equations, but is the conversion of sulphite into thiosulphate and consequent abstraction of sulphur from pentathionate.

This rapid conversion of sulphite into thiosulphate and consequent abstraction of sulphur from pentathionate affords, I think, the explanation of the influence of potassium sulphite in retarding the velocity and in diminishing the extent of the coloration when the ammoniacal silver nitrate test is employed in the presence of a sulphite. Sulphur is rapidly abstracted from the pentathionate, so that the solution becomes quickly diluted in respect of the pentathionate contained in it. Of the two other explanations which theoretically might be possible, the one, that the sulphite prevents the decomposition of the pentathionate, is shown by the above experiment to be incorrect, and the other, that the pentathionate is decomposed by the ammoniacal silver nitrate solution and the sulphite itself takes up the separated sulphur, seems improbable, for silver sulphide is an insoluble compound which would be preferentially formed.

These preliminary experiments establish the following facts: (1) Potassium sulphite and trithionate do not react in aqueous solution. (2) Potassium thiosulphate and trithionate react to an appreciable extent to form sulphite and tetrathionate and the merest trace of pentathionate. (3) Potassium thiosulphate and tetrathionate react in aqueous solution to form pentathionate, the resulting sulphite being immediately reconverted into thiosulphate. (4) Potassium sulphite rapidly abstracts sulphur from pentathionate when the two salts react in aqueous solution. (5) Solutions of potassium trithionate and tetrathionate containing a gram-molecular weight per litre are stable during twenty-four hours. Iodine has no immediate action on any or all of the salts, potassium trithionate, tetrathionate, and pentathionate. Potassium thiosulphate and sulphite when present with trithionate,

tetrathionate, or pentathionate, or a mixture of any or all of them, preserve their iodine titration-value, provided the thiosulphate or sulphite has not already reacted with the aqueous solution of such salt or salts.

Interaction in Aqueous Solution of Potassium Sulphite and Tetrathionate.

The aqueous solution of the sulphite and tetrathionate was contained in a tall cylinder of the capacity of 250–300 c.c., which was closed by a well-fitting indiarubber cork, through which passed a carbon dioxide entrance tube and an exit tube provided with a stop-cock. The potassium tetrathionate was dissolved in the cylinder in 175 c.c. of oiled water previously saturated with carbon dioxide, the quantity of the salt being weighed out separately each time. The sulphite solution was contained in small glass bulbs of about 30 c.c. capacity, from which the air was displaced by a stream of carbon dioxide. The sulphite solution was prepared by introducing into a dry 250 c.c. flask, from which the air had been displaced by carbon dioxide, the weighed quantity of the salt, and adding boiled out water (previously saturated with carbon dioxide) to the mark. The flask was provided with a cork, through which passed a glass tube, one end of which was connected with an apparatus generating carbon dioxide, and the other almost touched the surface of the liquid in the flask. The stop-cock of the carbon dioxide apparatus was always open, so that when the cork was removed a stream of the gas passed through the glass tube on to the surface of the sulphite solution. The bulbs were charged with the sulphite solution by withdrawing from the flask the requisite volume, 25 c.c., and running it into the bulbs, which were immediately afterwards sealed before the blowpipe. One such bulb was introduced into the cylinder containing the tetrathionate solution, and a similar one into a similar cylinder containing 175 c.c. of boiled water (previously saturated with carbon dioxide). The cork of each was replaced, and a rapid stream of carbon dioxide again passed through the liquids in the two cylinders. The bulbs were broken against the sides of the cylinders, and the contents of the cylinders well and quickly mixed partly by the stream of carbon dioxide and partly by shaking. The exact moment of breaking the bulb in the tetrathionate solution was recorded by releasing the seconds hand of a stop-watch. At intervals, 20 c.c. of the solution were withdrawn by a pipette and run into an iodine solution contained in small flasks, and the excess of iodine titrated with a solution of thiosulphate, 2 c.c. of which equalled

1 c.c. of the iodine solution. The initial sulphite titration was determined by ascertaining the iodine titration-value of 20 c.c. of the contents of the cylinder, which contained no dissolved tetrathionate, and determinations after varying intervals showed that with the above precautions this initial titration-value could be preserved for twenty-four hours, that is, the sulphite could be preserved from oxidation for so long a period at least.

In the account which follows, the strength of the iodine solution is given as a record of the concentration of the solutions in which the change was proceeding, for the sulphite initially contained in 1 c.c. of such solutions required as nearly as possible 1 c.c. of the iodine solution used in the titration, and the tetrathionate, and any other substance added to the solution, was present in equivalent proportion relatively to the sulphite or in some multiple or fraction thereof.

The Change Proceeds with the Formation of Potassium Thiosulphate in Quantities Equivalent to the Sulphite which has Entered into the Reaction.

The formation of thiosulphate was proved by estimating the iodine titration-value of a solution in which the change between tetrathionate and sulphite was proceeding, and also the acidity developed when the iodine titration was completed. Methyl-orange was used as indicator in the acidity determination, the blue colour of the starch iodide being first discharged with a drop of a thiosulphate solution.

The iodine solution contained 5.08 grams in 1000 c.c. In the first experiment, the proportions of sulphite and tetrathionate were equivalent; in the second, the proportions were $\text{K}_2\text{SO}_3 : \frac{1}{2}\text{K}_2\text{S}_4\text{O}_6$. In both cases it was found that:

$$A - S = T - A,$$

where

A = Actual iodine titration-value of the solution determined at varying intervals after mixing.

S = Iodine titration-value of sulphite then present, as calculated from the developed acidity.

T = Initial iodine titration-value of the solution.

Inasmuch as the iodine titration-value of a thiosulphate is only half that of its equimolecular proportion of sulphite, the diminution of the sulphite titration by an amount twice that of the diminution in the value of the iodine titration-value of the solution shows that thiosulphate has been formed in the solution in quantities equivalent to the sulphite which has reacted with tetrathionate.

The Conversion of Sulphite into Thiosulphate is Reversible.

At first it was attempted to prove the truth of this by determining the values of the percentage change at intervals of twenty-four, forty-eight, and seventy-two hours after mixing. However, the extent to which the conversion of sulphite into thiosulphate proceeds is a considerable proportion of the theoretically complete change, and in consequence, the velocity of change after these intervals, even supposing no limit short of complete conversion to be attainable, would be extremely small. By reason of this fact and the fact also that the solution might possibly become oxidised, the method was uncertain and was consequently abandoned.

In the absence of secondary reactions, if, with the exception of variation in the active masses of the substances entering into the reaction, the conditions under which a chemical change proceeds are constant, the velocity is directly proportional to the product of the active masses of the substances between which the change is proceeding. If no secondary reaction intervenes, the amount of transformation in a given interval of time, θ , can be calculated from the equation,

$$\frac{1}{A-x} - \frac{1}{A} = a\theta,$$

where

A represents the active masses of the substances present.

x = the quantity transformed in the interval of time, θ , and

a = a constant.

The comparison of the values of the percentage change of sulphite into thiosulphate after varying intervals of time from the first moment of mixing with the values for the same intervals calculated from the above equation by using for a its value as determined from the observed percentage change in the first interval of time, shows a retardation of the change in excess of that due merely to dilution.

The values for a solution of potassium sulphite and tetrathionate in equivalent proportions, the concentration of which corresponded with an iodine solution containing 5.08/2 grams in 1000 c.c., gave :

	Percentage change actually occurring.	Percentage change calculated from equation.	Differences.
$\frac{1}{4}$ hour after mixing	29.5	29.5	—
$\frac{3}{4}$ " " "	41.9	45.5	3.6
$\frac{5}{4}$ " " "	50.2	55.6	5.4
1 " " "	55.7	62.6	6.9

The secondary reactions which are theoretically possible in a solution in which sulphite and tetrathionate are reacting one with

another are : the reverse change between thiosulphate and trithionate, the formation of pentathionate by interaction of tetrathionate and thiosulphate, and its subsequent reconversion into tetrathionate by the action of sulphite. The preliminary experiments have shown that potassium trithionate and thiosulphate do react to form tetrathionate and sulphite, and that potassium tetrathionate and thiosulphate react to form pentathionate. They have also shown how rapidly potassium pentathionate and sulphite interact. It will be subsequently shown that pentathionate is not permanently formed in a solution in which potassium tetrathionate and sulphite react in equivalent quantities. The interaction of trithionate and thiosulphate would account for a retardation of the velocity of the direct change between tetrathionate and sulphite in excess of that occasioned merely by dilution, and, from the fact disclosed by the preliminary experiments that potassium trithionate does react with thiosulphate to form sulphite and presumably tetrathionate, may, I think, be regarded as in the main responsible for the retardation, in excess of that occasioned by dilution, in the velocity with which the direct change between tetrathionate and sulphite proceeds. In other words, the change between tetrathionate and sulphite of potassium is a reversible one. However, certain results to be mentioned later are quite inconsistent with the supposition that the change is a simple reversible one uncomplicated by any secondary reactions. As will be shown later, the addition to the system of either potassium trithionate or thiosulphate, instead of retarding, accelerates the velocity of chemical change in the first hour, although the addition of either of these substances reduces the limit values.

With the view of gaining some conception of the approximate limit value for the change between sulphite and tetrathionate, portions of 20 c.c. of a solution in which the change was proceeding were sealed up in small glass bulbs, from which the air had been displaced by carbon dioxide. The solution corresponded with an iodine solution containing 5.08/2 grams in 1000 c.c., and the sulphite and tetrathionate were present in equimolecular proportions. The values of the percentage change at the end of twenty-four hours, forty-eight hours, and eight days were determined :

24 hours	from first mixing,	the percentage change was	91.4
48	"	"	92.7
8 days	"	"	93.1

In each case, the titrated solution was distinctly acid. The values seemingly point to a limit value somewhat less than 95 per cent.

Pentathionate is not Permanently Formed in the Solution when Potassium Sulphite and Tetrathionate react in Equivalent Proportions in Aqueous Solution.

The preliminary experiments have already shown how rapidly sulphite abstracts sulphur from pentathionate, the sulphite itself becoming converted into thiosulphate. The pentathionate, if formed when potassium sulphite and tetrathionate react in equimolecular proportions in aqueous solution, would more probably be found in a solution in which the change had been proceeding for some time. Accordingly, having sought in vain for its presence in portions of solutions in which less than 50 per cent. of the sulphite had been converted into thiosulphate, solutions in which the change had proceeded for twenty-four and forty-eight hours respectively were examined. Portions of 10 c.c. of the solutions when tested with the ammoniacal silver nitrate solution did not in either case show any darkening within the first two hours. Eighteen hours after adding the ammoniacal silver nitrate solution a darkening had developed, the intensity of which about equalled that developed in a quarter of an hour in a solution of potassium pentathionate containing 0.0361 gram in 100 c.c. The inference to be drawn is, apparently, that, until the sulphite present in the solution had become oxidised by exposure to the air, no pentathionate was permanently formed in the solution. When potassium sulphite and tetrathionate in equivalent proportions react in aqueous solution, pentathionate is not permanently formed in the solution, provided the excess of sulphite is protected from oxidation.

The Effect of Varying the Mass of the Tetrathionate, the Mass of the Sulphite Initially Present Remaining Constant.

The sulphite present corresponded with an iodine solution containing 5.08/2 grams in 1000 c.c. The tetrathionate present was in *A*, the equivalent proportion of the sulphite, in *B*, half the equivalent proportion, and in *C*, twice the equivalent proportion. The values for the percentage change were :

	<i>A.</i> $\text{K}_2\text{SO}_3 : \text{K}_2\text{S}_4\text{O}_6$	<i>B.</i> $\text{K}_2\text{SO}_3 : \frac{1}{2}\text{K}_2\text{S}_4\text{O}_6$	<i>C.</i> $\text{K}_2\text{SO}_3 : 2\text{K}_2\text{S}_4\text{O}_6$
$\frac{1}{4}$ hour after mixing	29.9	15.8	53.0
$\frac{1}{2}$ hour „ „	41.6	23.3	68.3
$\frac{3}{4}$ hour „ „	50.2	28.7	75.7
1 hour „ „	55.8	32.7	80.7
24 hours „ „	90.8	50.5	100.0

These values are the percentage conversion of sulphite into thio-sulphate actually occurring. In the case of *B*, in order that they should express the percentage of the theoretically possible conversion,

they would require to be multiplied by two. In the case of *B* and *C*, the total theoretically possible conversion of sulphite into thiosulphate has taken place; the slight excess of 50·5 over 50·0 is, of course, due to oxidation. In *C*, where, after twenty-four hours, sulphite was no longer present, it was to be expected from the preliminary experiments that pentathionate would be found. The ammoniacal silver nitrate test gave an immediate darkening with 10 c.c. of the solution (*C*); pentathionate had been formed in considerable quantities.

Effect of the Presence in the System $K_2SO_3-K_2S_4O_6$ of (a) Potassium Trithionate, (b) Potassium Thiosulphate, in Quantities Equivalent to the Sulphite.

The concentration of the solution in respect of the sulphite initially present corresponded with an iodine solution containing 5·08/2 grams in 1000 c.c. The tetrathionate and the trithionate or thiosulphate initially present was the equivalent proportion of this quantity of sulphite:

At the end of	the percentage conversion of sulphite into thiosulphate was	$K_2SO_3 : K_2S_4O_6$		
		$K_2SO_3 : K_2S_4O_6$	$K_2SO_3 : K_2S_2O_3$	$K_2SO_3 : K_2S_4O_6 : K_2S_2O_3$
$\frac{1}{4}$ hour		29·0	34·8	40·8
" $\frac{1}{2}$ "	" "	41·6	48·8	53·7
" $\frac{3}{4}$ "	" "	50·2	56·2	60·2
" 1 "	" "	55·8	61·2	64·8
" 48 hours	" "	92·3	90·0	87·0

The increase in the values for the percentage change occurring during the first hour, when thiosulphate or trithionate is present, over the corresponding values, when sulphite and tetrathionate interact in the absence of these substances, is noticeable, and clearly shows that the nature of the reaction between potassium tetrathionate and sulphite cannot be a simple reversible change. The presence of products of the change accelerates the rate of chemical change. On the other hand, the values for the interval of forty-eight hours are in both cases smaller than the corresponding percentage (92·3) for the system $K_2SO_3 : K_2S_4O_6$, and point to the reversibility of the change between potassium sulphite and tetrathionate. The fact that thiosulphate does in certain circumstances react with tetrathionate, whereas trithionate does not react with either sulphite or tetrathionate, may account for the difference in the values of the percentage change when thiosulphate and trithionate are respectively present. Although thiosulphate and tetrathionate do not form pentathionate in the presence of sulphite, there must be a tendency to the formation of pentathionate, even if pentathionate is not actually momentarily formed, when thiosulphate and tetrathionate occur in a solution even

in the presence of sulphite. This tendency to the formation of, or the momentary formation of, pentathionate may conceivably account for the smaller percentage values when thiosulphate in place of trithionate is initially present.

Conclusions.

When potassium sulphite and tetrathionate are dissolved in the same aqueous solution, chemical change proceeds with the formation of thiosulphate in equimolecular proportions to the sulphite so converted. If the sulphite and tetrathionate are originally present in equimolecular proportions, the conversion of sulphite into thiosulphate does not proceed to completion, and pentathionate is not formed in appreciable quantities.

If the relative proportions in which the sulphite and tetrathionate are dissolved are either $\text{K}_2\text{SO}_3 : \frac{1}{2}\text{K}_2\text{S}_4\text{O}_6$ or $\text{K}_2\text{SO}_3 : 2\text{K}_2\text{S}_4\text{O}_6$, the theoretically complete conversion of sulphite into thiosulphate takes place, and in the latter case, when the sulphite has been wholly converted into thiosulphate, pentathionate is found in the solution in considerable quantity.

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