THE REACTION BETWEEN SODIUM SULPHITE AND SULPHUR.

By H. E. Watson and M. Rajagopalan.

Some years ago, owing to the increasing magnitude of the chrome-tanning industry in India, it was decided to investigate the possibilities of the commercial manufacture of sodium thiosulphate in the country. Of the various reactions available for producing this substance, the one between sodium sulphite and sulphur appeared most suited to local conditions, and a few experiments were sufficient to show that the reaction took place with great ease and yielded a very satisfactory product. In view of these promising results, a small plant was constructed and used to produce sodium thiosulphate in appreciable quantities.

Unknown to the authors, work on similar lines was being carried out in Calcutta, and in 1920, plant was erected in a Calcutta factory for producing thiosulphate from soda ash and sulphur.

While the experiments were in progress the English Patent Specification of Hutchins, Hargreaves and Dunningham [1] appeared in which a similar process was described, and attention was drawn to the low solubility of many salts in concentrated solutions of sodium thiosulphate, and to the accelerating influence of certain hydroxides and sulphides.

In order to elucidate certain phases of the reaction which could not be clearly followed when working on a larger scale, the small-scale experiments about to be described were undertaken and a brief account of them was given at the Indian Science Congress, 1922.

A paper by L. Hargreaves and A. C. Dunningham has since appeared [2] in which a process of making sodium thiosulphate is described and some curves showing the course of the reaction between sodium sulphite and sulphur are given. These are accompanied by very few details and relate entirely to very concentrated solutions.

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[1] E. P. 12,599 of 1915.

[2] *J. Soc. Chem. Ind.*, 1923, **42**, 147 T.

EXPERIMENTAL.

To 100 c.c. of water in a wide-necked 400 c.c. flask were added the required quantities of finely powdered sulphur and anhydrous sodium sulphite. It was difficult to obtain sodium sulphite in pure condition, but the variety finally selected was one made for photographic purposes containing on an average 92 per cent. of sulphite, the bulk of the impurity being sulphate together with some carbonate. The flask was closed with a rubber stopper through which passed a stirrer driven by a motor. It was immersed in a water-bath maintained at the required temperature to within 1°C; under these conditions it was found that the oxidation of sulphite during the course of an experiment was negligible.

Samples were withdrawn from the flask at definite intervals and analysed by Sutton's method.[1] This consists in adding 0·5 N sulphuric acid to a solution of the sample until it just begins to turn methyl orange red, indicating the conversion of the sulphite to bisulphite. This operation must be conducted slowly and with considerable care to avoid loss of sulphur dioxide. The suspended sulphur is filtered and washed, the solution being made up to 250 c.c. This solution is added to 20 c.c. of 0·1 N iodine solution until the latter is decolourised, and the hydriodic acid formed by the action of the iodine on the bisulphite titrated with 0·1 N sodium hydroxide using phenol phthalein as indicator. Although the method is not exceedingly accurate, it is rapid and convenient and the results appear to be comparable. In some cases the samples were not weighed so that only the ratio of thiosulphate to sulphite was determined, but in the earlier experiments the weight was taken and this allowed the conversion to be calculated from each of the three titrations, and more accurate values to be obtained. If a is the number of c.c. of decinormal iodine and b the number of c.c. of alkali required for the sample, the percentage of sulphite converted into thiosulphate is $100(3a-2b)/(3a-b)$, and in what follows we have termed this expression the percentage conversion. In making the calculation it is assumed that no sulphate or tri- or pentathionate was formed, as qualitative tests failed to show the presence of the latter substances; as already mentioned, quantitative measurements indicated that there was no appreciable oxidation during an experiment.

In a later series of experiments more satisfactory results were obtained by withdrawing the sample in a dry pipette of known weight, weighing the whole and washing the sample into a small Hirsch funnel

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[1] *Volumetric Analysis*, 10th edition, p. 344.

upon which the sulphur could be rapidly filtered and washed. The analysis was continued as above, but the last titration with alkali was carried out using methyl orange as indicator.

Preliminary experiments showed that the reaction proceeded at a convenient rate at temperatures in the nighbourhood of 70°, consequently most of the measurements were made at 60° and 80°.

Effect of rate of stirring.

Since one of the reacting substances is a solid, it was expected that diffusion would play a considerable part in determining the velocity and that consequently the effect of stirring would be considerable. Table I shows results obtained at 80° by stirring at different rates.

TABLE I.

Composition of Mixture	Rate of Stirring	Percentage Conversion after hours					
$Na_2SO_3 : S : H_2O$	r. p.m.	0·5	1	2	3	4	5
1 : 1 : 28	900–1000	13·2	27	44·1	55·2	62·4	...
	260–360	12·4	22·7	38·3	50·4	58·7	...
	40–60	12·4	22·5	34·9	45·6	54·3	...
1 : 1 : 7	900–1000	15·5	24·5	35·4	42·9	48·0	50·3
	35–60	14·2	19·1	24·7	32·6	...	...

Two different mixtures were used, the molecular composition being as shown in column 1. In the first of these sulphur alone was present in the solid form, in the second, some of the sodium sulphite was also undissolved. The effect of a change in the rate of stirring is well marked, but is not as great as might have been expected. In order to eliminate this effect as far as possible, the mixtures in all the subsequent experiments were stirred at a uniform rate of 900–1000 r.p.m.

These figures relate only to one particular stirrer in one particular flask. By using a more efficient stirrer the rate of conversion can be considerably increased, a conversion of 30 per cent. in three hours at 60° having been reached by a different type of stirrer at 2000 r.p.m., whereas with the stirrer for which the figures in Table I are given, the conversion at 1000 r.p.m. for the same temperature and time was only 16 per cent., the same mixtures being used in both cases.

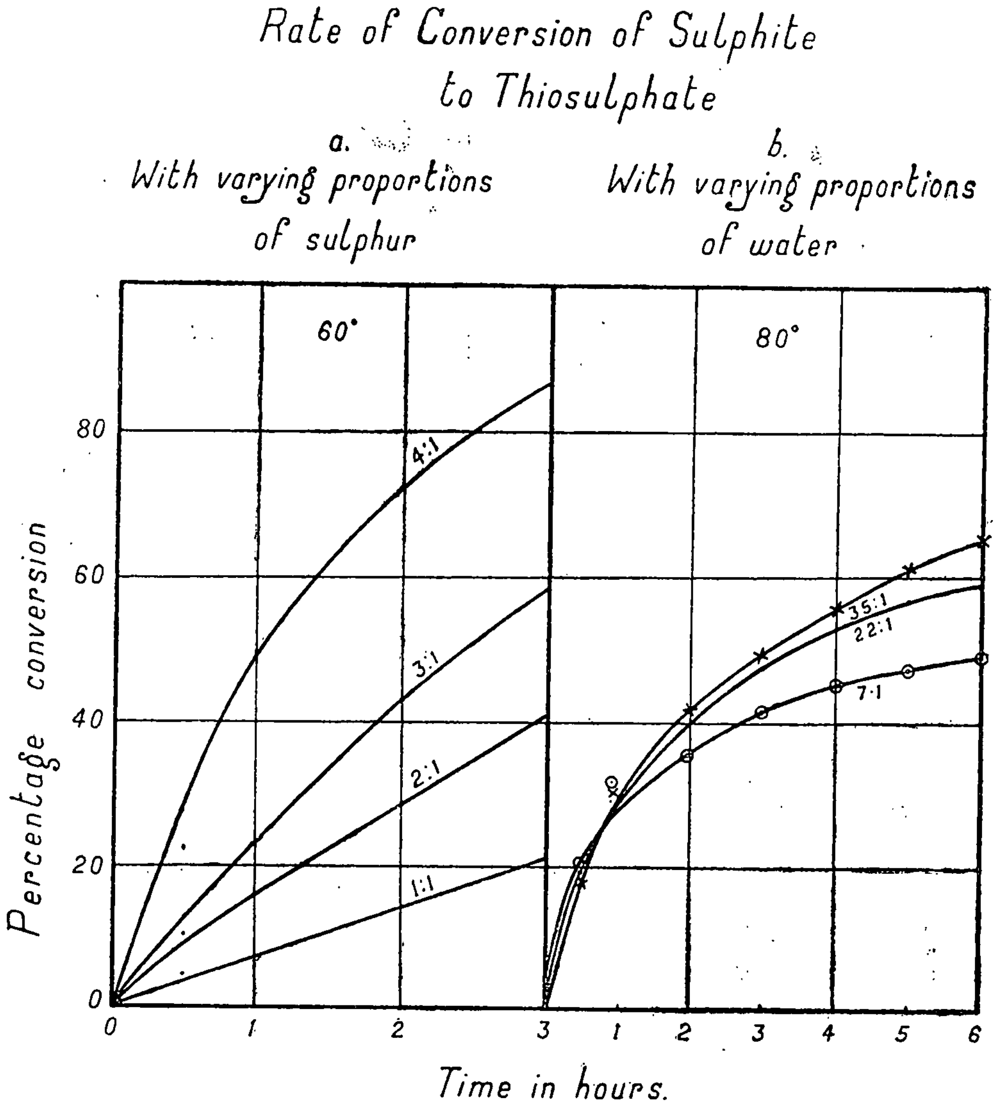
Effect of the quantity of sulphur.

In a heterogeneous reaction such as we are considering, it is to be expected that an increase in the quantity, or in other words of the surface, of the solid constituent, will cause an acceleration of the reaction. This we have found to be the case. Table II gives the percentage conversion obtained for mixtures with varying proportions of sulphur and the figure shows the results at 60° in the form of curves.

TABLE II.

Temperature	Composition of mixture $S : Na_2SO_3 : H_2O$	Percentage conversion after hours					
		0·5	1	2	3	4	5
60° ...	1 : 1 : 22	4·5	7·0	13·8	20·2	...	...
	2 : 1 : 22	10·0	15·8	27·4	40·4	...	...
	3 : 1 : 22	12·5	23·1	42·9	58·0	72·3	...
	4 : 1 : 22	22·1	48·7	71·5	86·8	...	...
80° ...	1 : 1 : 22	14	24·9	39·5	50	58·5	...
	4 : 1 : 22	...	100	100	...	...	...
80° ...	1 : 1 : 14	15·9	27·3	41	49·5	52·5	54·5
	2 : 1 : 14	38·5	52·0	79·3	85·4	90·1	93·4

It will be seen from the table that an increase in the amount of sulphur produces an increase in the velocity which is approximately proportional to the quantity taken except in the case of the last experiment at 60° in which the rate is abnormally high. It will also be observed that at 80°, quantitative conversion may be obtained in an hour by the use of four atomic proportions of sulphur.



Effect of the quantity of water.

The effect of different proportions of water has been studied at 80° for an equimolecular mixture of sodium sulphite and sulphur. The results are shown in Table III.

TABLE III.

Reaction between sodium sulphite and sulphur with different proportions of water at 80°.

Composition of mixture $H_2O : Na_2SO_3 : S$	Percentage conversion after hours					
	0·5	1	2	3	4	5
7 : 1 : 1	15·5	24·5	35·4	42·9	48·0	50·3
14 : 1 : 1	16·0	27·3	41·0	49·5	52·5	54·5
22 : 1 : 1	14·0	24·9	39·5	50·0	58·5	...
25 : 1 : 1	16·9	29·0	42·6	51·3	58·1	63·0
28 : 1 : 1	13·2	27·0	44·1	55·2	62·4	...
35 : 1 : 1	18·2	28·3	43·4	55·2	...	...
42 : 1 : 1	16·6	30·6	48·5	62·2	70·8	...
56 : 1 : 1	17·1	31·9	51·0	61·9	74·2	...

As these figures were rather irregular, a fresh series of determinations was made by Mr. M. Mulaney with the results shown in Table IV, and drawn as curves in the diagram.

TABLE IV.

Reaction between sodium sulphite and sulphur with different proportions of water at 80° C.

Composition of mixture $H_2O : Na_2SO_3 : S$	Percentage conversion after hours						
	0·5	1	2	3	4	5	6
7 : 1 : 1	20·9	32·9	35·9	40·7	44·1	46·8	49·2
7 : 1 : 1	20·8	30·2	36·9	42·6	45·7	47·9	49·5
14 : 1 : 1	...	29·4	40·3	45·1	47·6	52·0	54·8
22 : 1 : 1	18·9	27·9	38·8	46·3	51·6	55·5	58·2
22 : 1 : 1	20·8	31·0	41·1	48·8	53·3	56·9	58·4
35 : 1 : 1	18·7	31·2	42·9	49·0	56·0	61·6	65·7
35 : 1 : 1	17·7	28·7	39·4	48·4	54·2	60·5	63·2
70 : 1 : 1	24·6	...	52·5	...	66·3	...	...

From the above it is evident that, with apparatus employed, it is not possible to obtain results agreeing with each other more closely than within two or three per cent. when all the conditions are apparently the same. As this accuracy was sufficient for the purpose for which the experiments were originally made, further determinations were not conducted.

If the two series are compared, it will be observed that the initial rates of conversion shown in Table III are lower than those in Table IV, but that after four hours the order is reversed. The exact reason for this is not apparent, but it must be borne in mind that different apparatus and different materials were used in the two sets of experiments so that the results are not strictly comparable. It will be observed however, that in both cases the percentage conversion after some hours increases appreciably with the dilution of the solutions.

Effect of adding sodium sulphide.

In the patent under reference it is stated that the addition of alkalis or sulphides has an accelerating effect on the reaction. Hargreaves and Dunningham have published a curve showing that caustic lime increases the rate of the reaction perceptibly, but not to a very great extent. We have examined the effect of adding sodium sulphide to the reaction-mixture and the results are shown in Table V.

TABLE V.

Reaction between sodium sulphite and sulphur in presence of sodium sulphide:—$Na_2SO_3 : S : H_2O = 1 : 1 : 22$.

Temperature	Na_2S per cent. on sulphite	Percentage conversion after hours				
		0·5	1	2	3	4
60°	0	4·5	7·0	13·8	20·2	...
	1	6·7	10·6	21·0	30·1	36·7
	4	11·7	19·7	31·6	39·6	48·4
80°	0	14·0	24·8	39·5	50·0	58·5
	1	...	30·2	49·7	60·7	67·0

It will be seen that the influence of the catalyst is most marked at the lower temperature. At the higher temperature the effect must take place mainly in the initial stages of the reaction, for no sulphide could be detected in the solution after two hours.

It has been mentioned (p. 276) that the sulphite used contained carbonate. A few experiments were made in which the solution was neutralised before the reaction was started, but no change in the rate was observed.

The mechanism of the reaction.

The reactions studied may be divided into two classes, (*a*) those in which solid sodium sulphite is present, (*b*) those in which the sulphite is completely dissolved. The reactions with seven and fourteen molecules of water to one of sulphite belong to the first class, those with twenty-eight or more molecules to the second, while the one with twenty-two molecules belongs to the first class at the beginning and to the second at the end of the reaction.

When solid sodium sulphite is present initially, the concentration of the solution does not remain constant during the progress of the reaction, but, as has been shown by Hargreaves and Dunningham,[1] decreases rapidly as the quantity of thiosulphate increases, and it has been assumed by these authors that the decrease in reaction velocity is due to the decrease in concentration. An examination of our results appears to indicate, however, that this is not the case. This may be seen more clearly from Table VI in which the approximate composition of some of the more concentrated mixtures has been calculated by means of Hargreaves and Dunningham's data for solubility. As these are only given in the form of a curve it is not possible to make very accurate calculations. The table shows the percentage composition of the solutions obtained when equimolecular proportions of sulphur and sulphite are mixed with seven and twenty-two molecular proportions of water, initially, and after 0·5, 2 and 6 hours' stirring, the necessary data being taken from Table IV. The quantities of solid sulphite and sulphur present per 100 grams of solution are also given and finally the percentage of sulphur dissolving in each interval calculated by dividing the weight dissolved during that interval by the mean of the weights undissolved at the beginning and end of the interval and multiplying by 100.

The best method of determining the reaction velocity in mixtures such as the above would be to measure the quantity of sulphur dissolved in different times by a given volume of solution. As there appear to

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[1] *loc. cit.*

TABLE VI.

Composition of mixtures of sodium sulphite, thiosulphate, sulphur and water.

Molecular proportion			Time in hours			
			0·0	0·5	2·0	6·0
7 : 1 : 1	Solution	Thiosulphate per cent. ...	0·0	19·5	30·5	37·5
		Sulphite ,, ...	22·0	8	3	1·5
	Solid	Sulphite per 100 g. ...	64	59	39·5	30·5
		Sulphur ,, ...	19·8	15·0	10·8	7·8
	Per cent. of S dissolved ...		...	28	33	32
22 : 1 : 1	Solution	Thiosulphate per cent. ...	0·0	6·3	12	17
		Sulphite ,, ...	22·0	18	15	9
	Solid	Sulphite per 100 g. ...	3·2	7·5	4·2	0
		Sulphur ,, ...	6·35	5·15	3·65	2·45
	Per cent. of S dissolved		...	21	34	39

be no data regarding the densities of these solutions it is not possible to calculate this quantity from the figures in Table VI, and all that can be done is to obtain an approximation by measuring the weight dissolved by a given weight of solution.

It will be observed from the table that, after the first half hour, the solution with seven parts of water contains less sulphite than the other solution which might be expected to be the more dilute. In spite of this, the percentage of sulphur dissolved in corresponding periods of time in the two cases is approximately the same, bearing in mind the necessarily large errors arising from the method of calculation. In other words, the proportion of sulphur dissolving does not increase with the amount of sulphite in solution. The actual weight dissolving in the more concentrated sulphite solution is far more than in the other case, but it seems only reasonable to suppose that under the same conditions, the rate of solution of sulphur would be proportional to its surface, that is to say, before the surface has appreciably altered by solution, to its weight.

From these two examples it appears that the velocity of reaction is governed by the rate of solution of the sulphur and not by the concentration of the sulphite. This view is supported by reference to the results for the solutions in which all the sulphite was dissolved as shown in Tables III and IV. Instead of 'percentage conversion' one can read 'proportion of sulphur dissolved' and it will be seen that this proportion increases with the dilution. Hence it seems legitimate to assume that the reaction may be regarded as taking place in two stages, firstly, solution of the sulphur at a finite rate and secondly, combination of the dissolved sulphur with the sulphite at a rate very much greater than that of the first reaction.

The factors which determine the rate of solution of the sulphur appear to be very complex. From what has been already said, the rate appears to increase in dilute solution, but there is also some evidence that solution is favoured by the presence of thiosulphate. Two experiments were carried out under exactly similar conditions with 22 mols. of water to one each of sulphite and sulphur, and in one of them, one molecule of anhydrous thiosulphate was added to the mixture. In the experiment without thiosulphate the conversion in four hours was 24·7 per cent. while with thiosulphate it was 39·4 per cent. Too much importance must not however be attached to the result of a single experiment.

There is another factor of great importance. In Table VI it will be observed that the percentages of sulphur dissolved, although of the same order of magnitude, are not calculated for equal intervals of time. It might be expected that, if the rate of solution of the sulphur were independent of the concentration of sulphite, solution would take place according to a logarithmic law provided that the surface of the sulphur remained constant. Actually, the percentage dissolving in the first half hour in the first example given, is approximately equal to the percentage dissolving in four hours at a later stage, or in other words the rate of percentage solution is about 8 times as rapid initially as it is later. This may be explained by assuming that as the reaction proceeds the effective surface of the sulphur decreases.

In order to examine the validity of this assumption, an experiment was conducted in which sulphur which had been recovered from old experiments was used after washing and drying. The rate was found to be greatly lowered. Some fresh sulphur was then warmed with a mixture of sulphite and thiosulphate until 31 per cent. had been dissolved and another batch was warmed with sulphite only until 10 per cent. was dissolved. Both were washed and dried and used instead of the normal sulphur with the results shown in Table VII. In this table are also included two early results in which a comparison was made between 'flowers of sulphur' and 'roll sulphur' ground to pass through a 100-mesh sieve. These agree fairly well with each other but are not comparable with the other experiments.

TABLE VII.

Rate of reaction using different preparations of sulphur.

—	Percentage conversion after		
	1 hour	3 hours	5 hours
Normal sulphur (mean)	20·5	30·1	39·2
Do. 10 per cent. dissolved ...	6·2	12·2	18·3
Do. 31 do. ...	9·6	15·8	21·3
Do. about 40 per cent. dissolved...	6·1	12·9	19·8
Flowers of sulphur	27·3	49·5	54·6
Roll sulphur	29·6	47·0	53·4

On comparing the results for the partly dissolved specimens of sulphur it will be seen that the rates of solution are much lower than in the case of the original sulphur, but that there is no obvious connection between the rate and the amount of sulphur dissolved before using the sulphur. Further experiments in this direction are being conducted and some evidence has been obtained that the rate is largely influenced by the number of very fine particles present in any one sample of sulphur.

It was thought possible that treatment with sulphite might convert the crystalline into the amorphous form of sulphur and consequently all four samples were tested for their solubility in carbon disulphide. The original sulphur contained 6 per cent. of insoluble matter, the two specially treated samples 5 per cent. each and the recovered sample only 3 per cent. Microscopic examination revealed no obvious difference between any of the samples.

It is intended to continue the experiments under conditions more carefully regulated than has hitherto been the case in order to gain further insight into the mechanism of the reaction.

SUMMARY.

1. The reaction between sodium sulphite and sulphur takes place very readily above 60° in aqueous solution.

2. The reaction is accelerated by rapid stirring.

3. The addition of an excess of sulphur produces an acceleration approximately proportional to the quantity of sulphur. At 80°, with four molecules of sulphur and twenty-two of water to one of sulphite the reaction is complete in an hour.

4. Dilution of the solution produces a slight increase in the percentage conversion.

5. The velocity of the reaction appears to depend almost entirely upon the rate of solution of the sulphur and not to be governed by the concentration of the sulphite.

6. Preliminary treatment of the sulphur with sulphite solution reduces the rate at which it dissolves.

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