CXCVII.—*The Inter-relationships of the Sulphur Acids.*

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THIS investigation arose out of an attempt to explain the genesis of polythionates in the Wackenroder reaction and in the decomposition of thiosulphates by acid. It soon became clear that the reactions of many of the sulphur acids required further study before the formation of polythionic acids could be understood.

In all the reactions of the sulphur acids, the hydrogen-ion concentration plays a very important part and in great measure determines the path followed. Addition of acid, *i.e.*, hydrogen ions, to a system should, in accordance with the principle of Le Chatelier, favour reactions which remove hydrogen ions, whilst hydroxyl ions should produce exactly the opposite effect. These deductions are, on the whole, borne out by experiment.

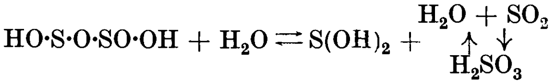
The method adopted in the theoretical portion of the present paper is to consider all reactions and give all equations in terms of the acids concerned, even although the reactions may occur in alkaline solutions. This has been done for the sake of simplicity and uniform treatment, and must not be taken to mean that the reactions may not follow an ionic course, although we think it probable that many of the reactions discussed do actually involve the non-ionised acids rather than their ions.

A number of equations have to be referred to frequently. These are given in the text in the positions where they are first considered. To each has been given a number by which it is referred to on subsequent occasions, and for convenience in reference all such equations are here collected in the order of their first appearance, equations mentioned only once not being included; *a* after the number of an equation signifies the reaction from left to right, *b* that from right to left.

$2S + 2H_2O \rightleftharpoons H_2S + (HO)_2S$ . . . . (I)

$S(OH)_2 + HO{\cdot}S{\cdot}O{\cdot}S{\cdot}OH \rightleftharpoons H_2S + H_2S_2O_5$ . . . . (II)

$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH \rightleftharpoons (HO)_2S{\cdot}SO_2$ . . . . (III)



$$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH + H_2O \rightleftharpoons S(OH)_2 + \begin{matrix} H_2O + SO_2 \\ \uparrow\downarrow \\ H_2SO_3 \end{matrix}$$ . . . (IV)

$S(OH)_2 + SO_2 \rightleftharpoons (HO)_2S{\cdot}SO_2$ . . . . (V)

$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH + (HO)_2S{\cdot}SO_2 \rightleftharpoons H_2S_2O_5 + H_2S_2O_3$ . . (VI)

$H_2SO_3 + H_2S_2O_5 \rightleftharpoons H_2SO_4 + H_2S_2O_4$ . . . . . (VII)

$H_2S_2O_3 \rightleftharpoons H_2SO_3 + S\ (2H_2S_2O_3 \rightleftharpoons 2H_2SO_3 + S_2)$ . . (VIII)

$2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6$ . . . . (IX)

$2H_2S_2O_3 \rightleftharpoons H_2O + H_2S_4O_5$ . . . . (X)

$$H_2S_2O_7 + H_2S \rightleftarrows H_2S_3O_6 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (XI)$$
$$H_2S_3O_6 + S \rightleftarrows H_2S_4O_6 \ (2H_2S_3O_6 + S_2 \rightleftarrows 2H_2S_4O_6) \quad . \quad (XII)$$
$$H_2S_4O_6 + S \rightleftarrows H_2S_5O_6 \ (2H_2S_4O_6 + S_2 \rightleftarrows 2H_2S_5O_6) \quad . \quad (XIII)$$
$$H_2S_3O_6 + H_2S_2O_3 \rightleftarrows H_2S_4O_6 + H_2SO_3 \quad . \quad . \quad . \quad . \quad . \quad (XIV)$$
$$H_2S_4O_6 + H_2S_2O_3 \rightleftarrows H_2S_5O_6 + H_2SO_3 \quad . \quad . \quad . \quad . \quad . \quad (XV)$$

In order to save space and avoid repetition, the experimental portion of the paper contains only the practical details of experiments, their connexion with the theoretical discussion being indicated by cross references. Any purely qualitative experiments which are discussed in the theoretical part are not, as a rule, referred to again in the experimental part.

The Hydrolysis of Sulphur. Sulphoxylic Acid.

It has been generally supposed that hydrogen sulphide and sulphurous acid are the first products of the hydrolysis of sulphur (Cross and Higgin, J., 1879, **35**, 249; *Ber.*, 1883, **16**, 1195) and may give rise to thiosulphuric or other sulphur acids.

This view is probably incorrect, for, just as the hydrolysis of chlorine results in the production of equivalent amounts of hydrogen chloride and hypochlorous acid, so the hydrolysis of sulphur should give equivalent amounts of hydrogen sulphide and sulphoxylic acid, $(HO)_2S$. The latter is doubtless a very unstable substance and would readily undergo further change.

Although neither free sulphoxylic acid nor its salts are known, there are two simple derivatives which are readily accessible. These are sodium formaldehydesulphoxylate and sodium hydrosulphite [hyposulphite]. We have shown that when sulphoxylic acid is liberated from the formaldehyde compound by hydrolysis it undergoes decomposition into hydrogen sulphide and sulphurous acid—a change analogous to that undergone by hypochlorous acid. If the hydrolysis occurs in presence of a lead, arsenic, antimony, stannous, bismuth, cadmium, nickel, cobalt, or zinc salt, the sulphide of the metal is precipitated. No acid, other than that present in the solution owing to hydrolysis, must be added in the case of zinc, nickel, or cobalt, otherwise the precipitate of sulphide fails to appear; and very little must be present in the case of cadmium. With salts of silver, copper, and mercury, reduction to metal occurs. This may occur also with arsenic and probably with antimony or bismuth, especially in absence of much acid, whilst, conversely, a little sulphide may be formed in the case of copper and silver in presence of much acid. Precisely what happens in such cases depends upon the relative rates of the oxidation of sulphoxylic acid to sulphurous acid or of its change into hydrogen sulphide and sulphurous acid. These rates are affected by concentration of reactants, acidity, and temperature (compare results with sodium hydrosulphite, $Na_2S_2O_4$, Firth and Higson, J., 1923, **123**, 1515; *J. Soc. Chem. Ind.*, 1923, **42**, 427T).

In absence of salts of heavy metals, the hydrogen sulphide acts upon the formaldehyde to some extent to yield trithioformaldehyde, which appears as white crystals or oily drops and is readily detected by its characteristic smell. The normal interaction of hydrogen sulphide and sulphurous acid leads to formation of sulphur and polythionic acids (see Expt. D).

On alkaline hydrolysis sulphur gives rise to polysulphide and thiosulphate (Gmelin, "Handbook of Chemistry," Watts's English Transl., 1849, II, 160; Auld, J., 1915, **107**, 480), both of which could result from further action of sulphur on previously formed sulphide and sulphite.

The acid hydrolysis of the formaldehydesulphoxylate occurs rapidly on heating, but is slow at the ordinary temperature; the actual rate depends also upon the acidity. The alkaline hydrolysis is extremely slow, but seems to follow a similar course to the acid hydrolysis, yielding sulphide and sulphite.

The action of formaldehydesulphoxylate on sodium plumbite solutions is slow at the ordinary temperature, but more rapid on heating. A mixture of metallic lead and lead sulphide is usually formed, a high concentration of sulphoxylate and high alkalinity being most favourable to the precipitation of lead sulphide. The reduction to metallic lead is due to the sulphoxylate, and not to the formaldehyde (Expt. A). In presence of plumbite, it is the formation of insoluble lead sulphide which accelerates the hydrolysis of the formaldehydesulphoxylate. Sulphur will produce a similar effect by converting the sulphite, formed on hydrolysis of the sulphoxylate, into thiosulphate. Thus it was found that, after an alkaline solution of formaldehydesulphoxylate had been boiled with sulphur and the polysulphide (much of which was, of course, due to alkaline hydrolysis of the sulphur) removed with lead acetate, the solution was no longer capable of bleaching methylene-blue. A similar alkaline sulphoxylate solution, after being boiled for the same length of time without sulphur, gave no precipitate with lead acetate and still had a strong bleaching action on methylene-blue (see also p. 1424). On boiling an alkaline solution of sodium hydrosulphite to which sodium plumbite has been added, a greyish-black precipitate of lead sulphide and metallic lead is obtained. The same reaction occurs at the ordinary temperature, but much more slowly. If the alkaline hydrosulphite solution is boiled and then cooled to room temperature before the sodium plumbite is added, an immediate black precipitate appears which consists of pure lead sulphide if only small quantities of hydrosulphite and plumbite are used in the experiment.

The work of Binz (*Ber.*, 1904, **37**, 3549), Bazlen (*Ber.*, 1905, **38**, 1067), and Reinking, Dehnel, and Labhardt (*ibid.*, p. 1069) leaves little doubt that sodium hydrosulphite, $Na_2S_2O_4$, is to be considered as the sodium salt of a mixed anhydro-acid derived from one molecule of sulphoxylic acid and one of sulphurous acid. At the ordinary temperature, it is so stable towards alkali that sodium hydroxide can be used to salt it out from its aqueous solution (Bernthsen and Bazlen, *Ber.*, 1900, **33**, 126). Bazlen (*loc. cit.*, p. 1057) showed that both before and after such salting-out the hydrosulphite had the formula $Na_2S_2O_4,2H_2O$. The experiments with lead, which have just been described, show that the hydrosulphite is hydrolysed slowly in alkaline solution even at the ordinary temperature, and the reactions then observed are the same as those obtained with sodium formaldehydesulphoxylate—both being the reactions of sulphoxylic acid or its decomposition products. If the solution is boiled before the plumbite is added, a precipitate of lead sulphide free from metallic lead can be obtained in the case of the hydrosulphite, because the sulphoxylate is converted into sulphide and sulphite as fast as it is formed. If the plumbite is present during the liberation of the sulphoxylate, some of the latter is oxidised by the plumbite before it is converted into sulphide and sulphite, and so a mixture of lead sulphide and lead is obtained. Alkaline solutions of sulphite give no reaction with plumbite under the conditions of these experiments, whilst thiosulphate in alkaline solution gives a very faint reaction which will be discussed in a later section (p. 1418).

The readiness with which sulphoxylic acid is converted into hydrogen sulphide and sulphurous acid in acid solution, or into sulphide and sulphite in alkaline solution, is quite sufficient to explain why hydrogen sulphide and sulphurous acid have been held to be the first products of the hydrolysis of sulphur. In view of these results, however, it is felt that there is every justification for considering that the primary reaction in the hydrolysis of sulphur, whether this occurs in acid or in alkaline solution, is correctly represented by the equation

$$2S + 2H_2O \rightleftharpoons H_2S + (HO)_2S \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Attempts to verify this equation directly have not been successful, but they do not disprove it.

The action of moist sulphur on silver and other metals, even at the ordinary temperature, is undoubtedly due to slow hydrolysis of the sulphur, which is accelerated by removal of the hydrogen sulphide as insoluble sulphide of the metal. Similarly, solutions of silver salts, or salts of other metals which form very sparingly soluble sulphides, are readily acted upon by sulphur on boiling. A quantitative experiment in which sulphur was digested with metallic silver in presence of chromic acid was in better agreement with reaction (I) than with a reaction $3S + 3H_2O \rightleftharpoons 2H_2S + H_2SO_3$, since approximately one molecule each of silver sulphide and sulphuric acid were formed (Expt. B).

When finely-ground rhombic sulphur was boiled with silver acetate solution, the alteration of the sulphur was very superficial owing to the dense, coherent film with which it became covered. This so effectively protected the sulphur that it was impossible to remove it completely even by long-continued extraction in a Soxhlet apparatus with benzene or carbon disulphide. Whether the film consisted of a mixture of silver sulphide and silver in the proportion to be expected from equation (I), could not therefore be determined.

The reactions $2S(OH)_2 = H_2S + H_2SO_4$ and $2S(OH)_2 = H_2S_2O_3 + H_2O$ look simple, but we can find no evidence that either of them occurs, although we have a certain amount of negative evidence against them. If sulphoxylic acid could undergo either of these changes, alkali should promote the changes, since both would correspond to a considerable increase in hydrogen ion. We find, however, that there is no sulphate produced when sodium formaldehydesulphoxylate is boiled with alkaline plumbite solution (Expt. C). Neither is any sulphate produced when sodium formaldehydesulphoxylate is hydrolysed in acid solution either alone or in presence of lead or arsenious salts (Expt. D). If the arsenious sulphide formed had resulted from the decomposition of thiosulphate, large amounts of sulphate would have been formed, as special experiments showed (Expt. E).

Long heating of alkaline solutions of sodium formaldehydesulphoxylate did not seem to lead to the formation of any thiosulphate; the sulphoxylate was apparently unchanged.

Sulphur separates at once when a strong hydrosulphite solution is added to concentrated hydrochloric acid, whereas when sodium thiosulphate is so added no separation of sulphur occurs for a long time (see p. 1430). If the sulphoxylic acid formed on hydrolysis of the hydrosulphite changed rapidly into thiosulphate, no separation of sulphur would therefore have been expected. That it does separate is not due to the presence of sulphite, for a solution containing an equimolecular mixture of sodium metabisulphite and thiosulphate did not yield any sulphur on being added to concentrated hydrochloric acid, except after long standing.

Foerster, Lange, Drossbach, and Seidel (*Z. anorg. Chem.*, **1923**, **128**, 268) assume that the reaction $2S(OH)_2 = H_2S_2O_3 + H_2O$ does occur, and at one time we thought the same, but we have reached the conclusion that there is no justification or need for the assumption. At first sight such a change seems to be indicated by the fact that sodium hydrosulphite, in absence of air, in neutral or faintly acid solutions, changes quantitatively into sulphite and thiosulphate (Meyer, *Z. anorg. Chem.*, 1903, **34**, 43; K. Jellinek and E. Jellinek, *Z. physikal. Chem.*, 1919, **93**, 325). The solid salt undergoes a similar change, and old specimens contain large amounts of thiosulphate. It is probable that in this change the thiosulphate is not formed directly from sulphoxylic acid, but by a more complex mechanism which is considered on p. 1411.

The mechanism of the change of sulphoxylic acid into hydrogen sulphide and sulphurous acid calls for comment. A reaction $3S(OH)_2 \rightleftharpoons H_2S + 2H_2SO_3$ seems improbable because (i) it would be termolecular although it actually occurs very readily, and (ii) it is more likely that dissimilar molecules are respectively oxidised and reduced. We suggest that it is sulphoxylic acid itself which is reduced, whilst its anhydro-acid, HO·S·O·S·OH, which is isomeric with thiosulphuric acid, is oxidised. This would give a reaction represented by the equation

$$S(OH)_2 + HO\cdot S\cdot O\cdot S\cdot OH \rightleftharpoons H_2S + H_2S_2O_5 \quad . \quad . \quad (II),$$

where the $H_2S_2O_5$ is pyrosulphurous acid. The reversal of this change would be the first step in the Wackenroder reaction (see p. 1440)

The position with regard to equilibrium (II), as disclosed by the reactions of formaldehydesulphoxylate with metallic salts, is somewhat peculiar. On the one hand, with arsenious chloride, increase in *acidity* favours precipitation of arsenious sulphide instead of elementary arsenic, which is formed when little free acid is present, but, on the other hand, in presence of sodium plumbite, increase in *alkalinity* favours formation of lead sulphide, the proportion of metallic lead which is precipitated increasing as the alkalinity decreases. These two results, although at first sight contradictory, can be explained on the basis of equation (II). The reaction would proceed from left to right with a considerable increase in hydrogen ions, for there can be little doubt that sulphoxylic acid would be a very weak acid just as hypochlorous acid is. Alkali should therefore favour the change into sulphide and sulphite, which agrees with the results of the plumbite experiments. In acid solution, high acidity might be expected to favour formation of anhydrosulphoxylic acid at the expense of sulphoxylic acid, and this also would accelerate the change of the latter into hydrogen sulphide and pyrosulphite. The effect of high acidity in favouring precipitation of arsenious sulphide, rather than of free arsenic, would then be intelligible. Increase in acidity would also tend to produce sulphur dioxide at the expense of either sulphurous or pyrosulphurous acid, and this also would hasten the decomposition of sulphoxylic acid. Reaction (I *b*) occurs with decrease of hydrogen ions, and so will be favoured by acidic conditions. It is this interaction of hydrogen sulphide and sulphoxylic acid which leads to the decomposition of sulphoxylic acid in acid solution in absence of metals which form insoluble sulphides. Such decomposition could be represented by the summation equation

$$2S(OH)_2 \rightleftharpoons H_2SO_3 + S + H_2O.$$

To postulate the existence of an anhydro-compound, such as HO·S·O·S·OH, under alkaline conditions may be considered unreasonable. This objection has been raised by Bucherer and Schwalbe (*Ber.*, 1906, **39**, 2814) to the unsymmetrical formula for sodium hydrosulphite. However, sulphoxylic acid may be expected to be a very weak acid, and anhydro- (or pyro-) or even meta-salts of weak acids can certainly exist in alkaline solution; for instance, the borates $Na_2B_2O_4,4H_2O$ and $K_2B_2O_4,2\frac{1}{2}H_2O$ can separate from solutions containing a large excess of alkali (Dukelski, *Z. anorg. Chem.*, 1906, **50**, 41).

Vogel and Partington (J., 1925, **127**, 1522) claim to have prepared solid, crystalline sodium sulphoxylate, Na_2SO_2, and sodium ethyl sulphoxylate, $NaEtSO_2$. The sodium sulphoxylate is said to be practically unattacked by boiling concentrated hydrochloric or sulphuric acid, although attacked by a hot mixture of fuming nitric acid and bromine. Such behaviour is most improbable, and our view is that these authors were actually dealing with more or less impure sodium sulphate. In any case it is certain that sodium sulphate is precipitated on addition of sulphuric acid to a solution of sodium compounds in absolute alcohol, and such addition was an important step in the recorded preparations.

Hydrosulphurous Acid.

The Factors which determine Colour in Simple Sulphur Compounds.—On the whole, the term "hydrosulphite," which is in fairly general use, would seem to be as good as any which has been suggested for the salt $Na_2S_2O_4$. "Hyposulphite," the official term, does not seem satisfactory, partly because this name has become so firmly attached to what is more correctly called thiosulphate, and partly because it is doubtful whether one could correctly apply it to $Na_2S_2O_4$, even if this complication did not exist. We consider that it is sulphoxylic acid, $S(OH)_2$ or H_2SO_2, which alone has any right to be called hyposulphurous acid. Since $H_2S_2O_4$ is a " mixed " anhydro-acid, it has no right to the name, as it does not belong to the simple sulphuric–sulphurous series at all, any more than thiosulphuric acid does.

We cannot discuss all the evidence for the unsymmetrical anhydro-acid structure of the hydrosulphites, but merely wish to direct attention to the fact that the action of various oxidising agents strongly indicates this structure. Mild oxidising agents, such as silver salts, normally oxidise hydrosulphite to sulphite, but the action of molecular oxygen is exceptional, for Meyer (*loc. cit.*) showed that in this case sulphite and sulphate are formed. His figures indicate that these would be in equimolecular proportion were it not for disturbances due to hydrolysis of hydrosulphite by the acid formed as the oxidation proceeds. This seems to agree particularly well with the unsymmetrical formula. We have found that, in solutions containing sufficient sodium carbonate to neutralise the acid as it is formed, the atmospheric oxidation of hydrosulphite proceeds smoothly as a unimolecular reaction (Expt. F).

Solutions of sodium hydrosulphite, as is well known, become yellowish-brown on acidification. With concentrated solutions, the colour may be as deep as, and very similar to, that of $N/10$-iodine. The smell of hydrogen sulphide is quite evident directly after acidification, but is soon masked by that of sulphur dioxide. This formation of hydrogen sulphide is not generally mentioned, and although Bernthsen (*Annalen*, 1881, **208**, 172) and Meyer (*loc. cit.*) mention that cadmium sulphide is precipitated when hydrosulphite solutions containing cadmium sulphate are acidified, they do not appear to have noticed the hydrogen sulphide itself. Sulphur eventually separates from the acidified solution, but the time which elapses before this occurs may be considerable. The colour persists longest when the acidification has been effected by sulphurous acid. If a strong sodium hydrosulphite solution is added to concentrated hydrochloric acid, one obtains but a momentary brown colour, and a precipitate of sodium chloride and sulphur separates at once.

The colour of acid hydrosulphite solutions has never been satisfactorily explained. It has usually been regarded as the colour of the free acid, but, according to present-day views, since the salts are colourless the acid should be colourless too, unless some change of constitution occurs after it is set free from its salts. The bright, clear, deep-coloured solutions do not at all give the impression of colloidal solutions of sulphur, a possibility which has been mooted (Abegg's Handbuch, 1908, II, Pt. 1, p. 262).

When considering a possible explanation of the colour, several other instances of colour in simple sulphur compounds or their solutions should be borne in mind. The chief of these are : (1) Sulphur itself—the much deeper colour of plastic sulphur as compared with crystalline sulphur is of interest. (2) Sulphur mono- and di-chlorides, which are yellow. (3) Sulphur tetrachloride, which has a brownish-red colour. (4) The polysulphides. (5) The yellow or greenish-yellow solutions obtained by saturating strong alkali-metal or ammonium bisulphite solutions with sulphur dioxide. (6) The yellow solutions obtained by the action of sulphur dioxide on thiosulphate solutions : yellow solids, $K_2S_2O_3,SO_2$ and $Rb_2S_2O_3,SO_2$ have recently been prepared by Foerster and Vogel (*Z. anorg. Chem.*, 1926, **155**, 161). (7) The yellow compounds of sulphur dioxide with potassium thiocyanate and with potassium iodide (Fox, *Z. physikal. Chem.*, 1902, **41**, 458; Ephraim and Kornblum, *Ber.*, 1916, **49**, 2007).

Since potassium bromide and chloride combine with sulphur dioxide to form colourless compounds, it would appear that the colour of the potassium iodide compounds is in some way due to the iodine. The potassium iodide–sulphur dioxide compound need not therefore be considered in the present connexion. The compound $KCNS,SO_2$ would, however, seem to owe its colour in some way to the attachment of sulphur dioxide to the sulphur of the thiocyanate.

According to the modern theories of valency, the sulphur atom in all its ordinary compounds is surrounded by an outer shell of 8 electrons. This is true of all the sulphur atoms in the following, among others : The S'' ion of the sulphides, the HS' ion, hydrogen sulphide, sulphites, sulphates, thiosulphates, and polythionates. The co-ordination number of these substances ranges from zero in the case of the S'' ion to 4 in the case of the sulphates. Nevertheless, all these compounds (unless a colour-giving positive ion is present) are colourless. The lack of visible colour seems, then, to depend upon the one common characteristic, the shell of 8 electrons, and is evidently independent of the state of the atom with respect to co-ordination.

The existence of the very stable sulphur hexafluoride shows that sulphur in suitable combination can have as many as 12 electrons in its outer shell. This compound also is colourless.

In sulphur tetrachloride, the sulphur atom would have an outer shell of 10 electrons, and since this compound has a brownish-red colour, it may well be that it is essentially the 10-electron sheath which determines visible colour in all the compounds we are considering. In potassium thiocyanate, the sulphur atom has the normal 8-electron sheath, but when it becomes co-ordinated with a molecule of sulphur dioxide in the compound $KCNS,SO_2$, it is then surrounded by a 10-electron sheath, and the compound is yellow.

Most of the other yellow sulphur compounds referred to above can be accounted for on this basis. The greenish-yellow sulphite solutions owe their colour to H_2SO_3,SO_2—perhaps better written as $H_2\left[{}^{O}_{O}S{}^{O}_{SO_2}\right]$, which is isomeric with pyrosulphurous acid, $H_2\left[{}^{O}_{O}SOS{}^{O}_{O}\right]$. The yellow colour of thiosulphate solutions which have been treated with sulphur dioxide would be due to $H_2\left[{}^{O}_{O}S{}^{O}_{S\cdot SO_2}\right]$. In both these cases the sulphur atom to which the sulphur dioxide becomes attached would have a 10-electron sheath.

When hydrosulphurous acid is liberated from its salts, it will be readily hydrolysed to sulphoxylic acid and sulphurous acid. The yellowish-brown colour is most probably due to a compound, $(HO)_2S\cdot SO_2$, obtained by the co-ordination of one molecule of sulphur dioxide with the sulphur atom of a molecule of sulphoxylic acid. It could also arise directly by a simple intramolecular change. This compound is isomeric with hydrosulphurous acid itself, which may be written $HO\cdot S\cdot O\cdot SO\cdot OH$. When sulphur dioxide is passed into a solution of sodium formaldehydesulphoxylate, a solution of precisely the same colour is obtained as from sodium hydrosulphite. The properties of the two solutions are similar, and the coloured compound may be the same in the two cases. It is possible, however, that the formaldehyde still remains attached in the one case.

It is noteworthy that formaldehyde removes the colour from solutions of all the above sulphur dioxide addition compounds owing to formation of the very stable formaldehydesulphurous acid.

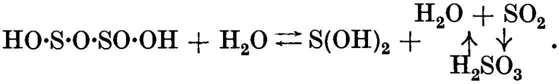
Sulphur monochloride, S_2Cl_2, would be expected on the above theory to be colourless. Its yellow colour may possibly be due to association in the liquid state, *i.e.*, co-ordination of one molecule with the sulphur atoms of other molecules.

The colour of sulphur itself and of the polysulphides is explicable on the basis of a colourless $S{<}^{S}_{S}$ molecule, with a structure similar to that assigned by Rankine (*Proc. Physical Soc.*, 1922, **35**, 33) to sulphur dioxide, in which all three sulphur atoms have 8-electron sheaths, or of an S_3 molecule of structure $S{=}S{-}S$, in which each sulphur atom would also have an 8-electron sheath. In hydrogen trisulphide, which is yellow, one of the sulphur atoms would have a 10-electron sheath, and so on. Hydrogen disulphide, which is presumably H·S·S·H, is colourless (Walton and Parsons, *J. Amer. Chem. Soc.*, 1921, **43**, 2539).

Sulphur tetrachloride is the only coloured sulphur compound which has been considered that does not contain sulphur–sulphur linkages, but it seems unlikely that such linkages in themselves have any great influence on the colour, since thiosulphates, polythionates, etc., in which such linkages occur, are colourless. The 10-electron sheath seems to be the important factor, although, of course, the actual colour of any particular compound must depend to some extent upon its structure and composition as a whole. It may well be that union of 10-electron sulphur with 8-electron sulphur promotes colour in a similar way to that assumed by Willstätter and Piccard (*Ber.*, 1908, **41**, 1465) in organic compounds with a *meri*-quinonoid structure.

The decomposition of hydrosulphurous acid can be briefly summed up thus :

$$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH \rightleftharpoons (HO)_2S{\cdot}SO_2 \quad . \quad . \quad . \quad . \quad (III)$$



$$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH + H_2O \rightleftharpoons S(OH)_2 + \overset{H_2O + SO_2}{\underset{H_2SO_3}{\uparrow\downarrow}} \quad . \quad . \quad (IV)$$

$$S(OH)_2 + SO_2 \rightleftharpoons (HO)_2S{\cdot}SO_2 \quad . \quad . \quad . \quad . \quad (V)$$

Whether direct rearrangement of the two isomeric forms of $H_2S_2O_4$ occurs, or whether one form is converted into the other *via* sulphoxylic acid formed by hydrolysis, it is not possible to say. Very likely both methods of change occur.

Since two sulphur atoms are directly united in $(HO)_2S{\cdot}SO_2$, its ready reduction to thiosulphate might be anticipated. K. Jellinek and E. Jellinek (*loc. cit.*) showed that hydrosulphurous and thiosulphuric acids are successive stages in the electrolytic reduction of sulphurous acid. Oxidation of $HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH$ by $(HO)_2S{\cdot}SO_2$ probably accounts for the change of hydrosulphite into thiosulphate and pyrosulphite in accordance with the equation :

$$HO{\cdot}S{\cdot}O{\cdot}SO{\cdot}OH + (HO)_2S{\cdot}SO_2 \rightleftharpoons H_2S_2O_5 + H_2S_2O_3 \quad . \quad (VI)$$

The change follows a bimolecular course (K. Jellinek and E. Jellinek, *loc. cit.*). The Jellineks' observation, that in presence of sodium bisulphite the rate of change is greater and roughly proportional to the square of the bisulphite concentration, is probably due to a stabilising effect of the sulphite on the two forms of hydrosulphurous acid in accordance with reactions (IV) and (V).

In acid hydrosulphite solutions there occur, superimposed on the above changes, the two reactions of sulphoxylic acid represented by equations (I) and (II). In addition, there is the possibility of polythionic acid formation, either by interaction of hydrogen sulphide and sulphurous acid or by decomposition of thiosulphate (see pp. 1416—17 and 1440). Polythionates appear to be always formed during the decomposition of hydrosulphurous acid (Foerster, Lange, Drossbach, and Seidel, *loc. cit.*, p. 278).

The fairly permanent, yellow colour, which remains after the yellowish-brown colour of $(HO)_2S{\cdot}SO_2$ has disappeared, is due to the sulphur dioxide–thiosulphuric acid complex.

Freshly acidified hydrosulphite has a most unpleasant smell suggestive of, but differing from, that of hydrogen sulphide, and not like a mixture of hydrogen sulphide and sulphur dioxide. It reminds one of sewer gas more than anything else, and it may well be the smell of sulphoxylic acid.

The Autoxidation of Sulphurous Acid.

It is known that in absence of air solutions of sulphurous acid slowly undergo a change which is generally represented by the equation $3H_2SO_3 = 2H_2SO_4 + S + H_2O$. This change is greatly accelerated by a high temperature or exposure to light.

Foerster, Lange, Drossbach, and Seidel (*loc. cit.*) have recently made a careful and exhaustive study of this reaction. With some of the theoretical conclusions of these authors we cannot agree, and we shall briefly explain our own views without adducing full details of the evidence. We agree with them (*loc. cit.*, p. 267) that two different molecules must be concerned in the oxidation and reduction which is the first step in the autoxidation, but not with their suggestion that these are two different forms of the HSO_3' or S_2O_5'' ions reacting according to the equations: $2HSO_3' \longrightarrow SO_4'' + H_2SO_2$; $S_2O_5'' \longrightarrow SO_4'' + SO$, where H_2SO_2 is sulphoxylic acid and SO its anhydride.

We consider that the reaction

$$H_2SO_3 + H_2S_2O_5 \rightleftharpoons H_2SO_4 + H_2S_2O_4 \quad . \quad . \quad . \quad \text{(VII)}$$

is far more probable, this equation being regarded as applying to the reactions of the respective ions as well as to the non-ionised acids, as mentioned on p. 1401. We have already (p. 1406) given reasons for the view that pyrosulphurous acid is the oxidising agent in the Wackenroder reaction, and if so, it is probably the oxidising agent in the autoxidation reaction also. Solutions of sulphurous acid appear to contain most of their sulphur dioxide as such (Wright, J., 1914, **105**, 2907), whilst solutions of alkali-metal bisulphites contain some pyrosulphite (metabisulphite) (Baly and Bailey, J., 1922, **121**, 1813; Getman, *J. Physical Chem.*, 1926, **30**, 266). It is not unreasonable to suppose that there is some pyrosulphurous acid even in " sulphurous acid " solutions. Since sulphate appears from the very beginning of oxidation, sulphurous acid is probably the substance oxidised. $H_2S_2O_4$, hydrosulphurous acid, is then the most probable product of reduction of the pyrosulphurous acid.

Since the hydrosulphurous acid is unstable under the prevailing conditions, it does not accumulate but rapidly undergoes further change (p. 1411). This makes the proof of its formation difficult.

Jungfleisch and Brunel (*Compt. rend.*, 1913, **156**, 1719) stated that they had obtained all the reactions for hydrosulphite at the stage of the autoxidation just prior to the separation of sulphur. Foerster and his colleagues (*loc. cit.*, pp. 277, 288, 293, and 300) could only partly confirm this, although they admitted that in some cases small quantities of hydrosulphite are formed at some stage of the reaction.

The only reaction for hydrosulphite which can be obtained in these sulphite solutions undergoing autoxidation is the bleaching of indigo, which is very delicate (but see p. 1439).

Sulphur dioxide co-ordinated with thiosulphate or iodide $[H_2S_2O_3\cdot(SO_2)_x;\ HI(SO_2)_x]$ may also be able to oxidise sulphurous acid and perhaps more rapidly than does pyrosulphurous acid. This would be represented by $H_2SO_3 + [SO_2] = H_2SO_4 + [SO]$, where square brackets indicate a co-ordinated condition; such a reaction could account for the remarkable way in which iodide or thiosulphate accelerates autoxidation of sulphurous acid (Foerster *et al.*, *loc. cit.*, pp. 266—269).

If our views expressed on pp. 1409—10 are correct, the yellow bisulphite solutions contain H_2SO_3,SO_2, in which the sulphur dioxide is co-ordinated in a similar way to that present in the iodide and thiosulphate complexes. The colour and other indications suggest that this form of pyrosulphurous acid is practically absent from sulphurous acid solutions, especially weak ones, which nevertheless undergo slow autoxidation. It seems likely, therefore, that it is the colourless pyro-acid form of $H_2S_2O_5$ (corresponding to the solid, colourless pyrosulphites or metabisulphites) —$SO_2H\cdot O\cdot SO_2H$— which is normally responsible for the first step in the autoxidation of sulphurous acid solutions (reaction VII), and that it is the pyro-acid form of hydrosulphurous acid —$H\cdot SO_2\cdot O\cdot S\cdot OH$— which is produced in this first step.

Some of the pyro-acid form of hydrosulphurous acid undergoes rearrangement to the coloured form, $H_2SO_2\cdot SO_2$, and the two forms then react to yield thiosulphate and pyrosulphite (reaction VI).

The middle phase of the autoxidation of sulphurous acid is essentially the decomposition of thiosulphuric acid (discussed on pp. 1416—40). Trithionic acid, one of the first products of this decomposition, gradually yields tetra- and penta-thionic acids as the concentration of sulphurous acid diminishes with the progress of the autoxidation. The polythionic acids finally decompose in their turn, and the final products of the autoxidation are sulphur and sulphuric acid.

On account of this polythionic acid formation during autoxidation, tri- and tetra-thionic acids are almost always present in old sulphurous acid solutions, whether these have been entirely protected from atmospheric oxidation or not. As the thionic acids are slowly decomposed in acid solution, the amount surviving in any given case depends upon the age and composition of the solution (Expt. G, Table I).

No separation of sulphur occurs for a long time, because the excess of sulphurous acid stabilises both the sulphoxylic and the thiosulphuric acids by yielding with them the sulphur dioxide addition complexes. Formation of thiosulphate from sulphite and sulphur, according to reaction (VIII), is greatly facilitated, and also the formation of trithionate in accordance with reaction (IX), the hydrogen sulphide being removed by interactions with sulphoxylic acid (reaction I), with pyrosulphurous acid (reaction II), or with the sulphur dioxide of the sulphur dioxide–thiosulphate complex. The last reaction could be written $H_2S + [SO_2] = S(OH)_2 + S$, although it only occurs when the sulphur dioxide is combined or co-ordinated in a suitable manner (indicated by the square brackets).

We, like Foerster, suppose that the autoxidation involves the formation of thiosulphate and the breakdown of this by way of the polythionates. Our views differ more particularly as to the manner in which the thiosulphate originates and decomposes. We can find no evidence for the direct conversion of sulphoxylic acid into thiosulphuric acid, which is postulated by Foerster, and do not believe that it occurs (see pp. 1405, 1406, and 1439). The breakdown of thiosulphuric acid will be considered in the next section. Foerster considers that pentathionic acid is the first polythionic acid to be formed from thiosulphuric acid, whereas we consider that trithionic acid is first formed (reaction IX).

During the stage of autoxidation (reactions VII and VI), where thiosulphate is forming, the acidity or hydrogen-ion concentration increases, and addition of acid is consequently unfavourable to the reaction. On this account, bisulphite solutions undergo autoxidation much more rapidly than do sulphurous acid solutions.

This effect of the hydrogen ion is connected with its influence on the equilibria $H^{\cdot} + HSO_3' \rightleftarrows H_2SO_3 \rightleftarrows H_2O + SO_2$. The more acid the solution, the greater the proportion of sulphur dioxide present, and since the autoxidation becomes correspondingly slower, this favours the view that sulphur dioxide is not one of the primary reactants. The well-known photochemical change $3SO_2 = 2SO_3 + S$ will not take place if the gas is absolutely dry (Coehn and Becker, *Z. physikal. Chem.*, 1910, **70**, 89), so that possibly even in this case the reaction follows a similar course to that outlined above, in the film of moisture adsorbed on the surface of the containing vessel.

Liquids other than water may be able to bring about the reaction, as in the somewhat similar case of the interaction of hydrogen sulphide and sulphur dioxide (Matthews, J., 1926, 2270). The view that pyrosulphurous acid is one of the primary reactants in the autoxidation of sulphurous acid is strengthened by the observations of Bennett (J., 1922, **121**, 1794), who found that sulphur, or even hydrogen sulphide, was liberated when sodium sulphite or pyrosulphite, in the solid state or in saturated solution, was added to hot concentrated sulphuric or phosphoric acid. Sulphur dioxide or its saturated solution in water would not act in this way. Under Bennett's conditions, the various stages in the autoxidation are passed through very rapidly, and it is not surprising that only the use of salts enables a sufficient concentration of pyrosulphurous acid to be obtained to make this possible.

It seems probable that, whenever sulphurous acid is reduced in presence of water, the reduction proceeds normally through the stage of hydrosulphite and not directly to sulphur or hydrogen sulphide. These would be products of decomposition of hydrosulphurous, sulphoxylic, or thiosulphuric acid. In certain cases the last may be the second step in the reduction, as in the electrolytic reduction already referred to (K. Jellinek and E. Jellinek, *loc. cit.*). Instances of reactions involving sulphurous acid which can be so accounted for are numerous (Smythe and Wardlaw, *Proc. Durham Phil. Soc.*, 1913—14, **5**, 187; Durrant, J., 1915, **107**, 622; Wardlaw and Clews, J., 1920, **117**, 1093; Wardlaw, Carter, and Clews, *ibid.*, p. 1241; Wardlaw and Pinkard, J., 1922, **121**, 210; Stewart and Wardlaw, *ibid.*, p. 1481; Rogers, J., 1926, 254; Carter, *J. Soc. Chem. Ind.*, 1926, **45**, 207T; Wardlaw, *ibid.*, p. 210T).

Bichowsky (*J. Amer. Chem. Soc.*, 1922, **44**, 116) has shown that at high temperatures (527—613° Abs.) the hydrolysis of sulphur leads to equilibria involving hydrogen sulphide, sulphur dioxide, and sulphuric acid. These can be regarded as resulting from a combination of the hydrolytic equilibria occurring at the ordinary temperature with the autoxidation equilibria.

The Decomposition of Thiosulphuric Acid.

Numerous investigations on the action of acids upon thiosulphates have been published during the last few years, since we commenced our own experiments, and we disagree with many of the conclusions. We find that thiosulphuric acid decomposes according to the three reversible reactions

$$H_2S_2O_3 \rightleftharpoons H_2SO_3 + S \quad . \quad . \quad . \quad . \quad . \quad . \quad (VIII),$$
$$2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6 \quad . \quad . \quad . \quad . \quad . \quad (IX),$$
$$2H_2S_2O_3 \rightleftharpoons H_2O + H_2S_4O_5 \quad . \quad . \quad . \quad . \quad . \quad (X).$$

Only reaction (VIII) is usually mentioned in text-books.

Reaction (IX).—The fact that hydrogen sulphide is invariably formed in small amounts when acid is added to thiosulphate solutions has escaped notice almost entirely. Spring and Levy (*Bull. Acad. roy. Belg.*, 1876, **42**, 103; Spring's collected researches, 1923, Vol. II, p. 1028) observed it, and so did Colson (*Bull. Soc. chim.*, 1880, **34**, 66). Colson attempted to discover the nature of the reaction and determined the ratio of hydrogen sulphide and sulphuric acid formed. He found that this was variable and seems to have concluded that the hydrogen sulphide was formed by the action of nascent sulphur on hot water. Of later workers, only Foerster, Lange, Drossbach, and Seidel (*loc. cit.*, pp. 245, 307) allude to it. They suppose that hydrogen sulphide is formed by a minor side-reaction, $H_2S_2O_3 + H_2O \rightleftharpoons H_2SO_4 + H_2S$, and do not bring this into their scheme of polythionate formation. The presence of hydrogen sulphide in standard sodium thiosulphate solutions has been attributed by Schulek (*Z. anal. Chem.*, 1926, **68**, 387) to bacterial action.

We find that hydrogen sulphide is always produced when acids or even water alone acts upon sodium thiosulphate. The gas is evolved if carbon dioxide is bubbled through, or if the thiosulphate is warmed with boric acid, whilst stronger acids liberate it readily. Little or no sulphuric acid is produced unless the mixture is boiled for a long time. It then results from the hydrolysis of tri- and tetra-thionic acids (Expt. H).

According to Jellinek (*Z. physikal. Chem.*, 1911, **76**, 257; see also Kolthoff, *Rec. trav. chim.*, 1924, **43**, 216) the oxy-acids of sulphur can be arranged in order of increasing strength in the series

$$H_2SO_3, H_2S_2O_4, H_2S_2O_3, H_2SO_4, H_2S_2O_6, H_2S_3O_6.$$

Di- and tri-thionic acids are of about the same strength, and so are thiosulphuric and sulphuric acids, whilst sulphurous acid is much the weakest of the series; hydrogen sulphide is still weaker. Reactions (VIII) and (IX) correspond to a definite decrease of hydrogen-ion concentration when proceeding from left to right. They should therefore tend to occur in acid solution, as we find to be the case, whilst they should be reversed in alkaline solution, which is true also.

That polythionic acids are formed by the action of acids on thiosulphates is fairly well known: Chancel and Diacon (*Compt. rend.*, 1863, **56**, 710; *J. pr. Chem.*, 1863, **90**, 55) seem to have been the first to observe it. We believe that our experiments show that reaction (IX) is the most important one by which these acids are formed. It is true that the amount of hydrogen sulphide liberated is very small in proportion to the amount of polythionic acids formed, but this is because reaction (VIII) is that which normally occurs to the greatest extent when acid acts upon thiosulphate. The hydrogen sulphide is thus liberated in presence of a large amount of sulphurous acid and destroyed by the same reactions which occur in the Wackenroder solution, which will be considered presently.

On this basis, trithionic acid becomes a primary, if not *the* primary, thionic acid produced.

The argument used by Foerster and Vogel (*loc. cit.*, p. 173) to show that penta- and not tri-thionic acid must be the primary thionic acid is unsound. According to our scheme, trithionic acid, formed by reaction (IX), combines with sulphur, formed by reactions (VIII), (II), and (I), to yield tetra- and penta-thionic acids. These are also formed by interaction with thiosulphate according to reactions (XIII) and (XIV). The fact that more thiosulphate than sulphite was consumed in Foerster and Vogel's experiments can thus be quite satisfactorily accounted for on the basis of our views.

Tetra- and penta- as well as tri-thionic acids are formed in the action of acids on thiosulphates, but the points which arise in this connexion will be discussed in the next section, which deals with the Wackenroder reaction.

Spring and Levy (*loc. cit.*) are the only authors who have attached any importance to the liberation of hydrogen sulphide, and who have assumed that polythionates result from trithionate formed in the manner just indicated. Of the greatest significance in this connexion is the fact that in alkaline solution the converse change occurs, alkali sulphide and trithionate reacting to form thiosulphate (Chancel and Diacon, *loc. cit.*).

We consider that there is overwhelming evidence that a reaction $H_2S_2O_3 + H_2O \rightleftharpoons H_2SO_4 + H_2S$ does not occur in either direction. The direct formation of sulphuric acid and hydrogen sulphide from thiosulphuric acid would correspond to a small increase in hydrogen ions, so that, if it is possible, it should be favoured by alkali and hindered by acid, whilst the formation of thiosulphate from sulphate and sulphide should be favoured by acidic conditions. Now we have found that in alkaline solutions mixtures of sulphate and sulphide do not react to form thiosulphate, nor does thiosulphate yield sulphate and sulphide [see Expt. I, (i), (ii), and (vi)]. There seem to be only two ways of explaining these facts : either (*a*) the chemical inertia of the system is so great that unstable conditions persist more or less indefinitely, or (*b*) thiosulphate is not directly related to sulphate and sulphide in the manner indicated by the above equation.

There is considerable evidence in support of (*b*). The precipitation of sulphides of metals by the action of soluble thiosulphates on solutions of their salts, or by decomposition of previously-formed thiosulphates of the metals, is usually supposed to occur in such a way as to give sulphide and sulphate directly, *e.g.*, $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$, and a similar decomposition of thiosulphuric acid has been inferred. The same result could, however, be reached *via* the trithionate, *e.g.*,

$$2Ag_2S_2O_3 = Ag_2S + Ag_2S_3O_6\,;\ Ag_2S_3O_6 + 2H_2O = Ag_2S + 2H_2SO_4.$$

Since the trithionates of the heavy metals are nearly as unstable as the thiosulphates, it is difficult to settle this point with simple thiosulphates, although Fogh (*Compt. rend.*, 1890, **110**, 524) has shown quite clearly that when lead thiosulphate is boiled with water it yields, in the first instance, sulphide and trithionate. Fogh states that this decomposition into trithionate can occur quantitatively without any side reactions, but we have always found some decomposition of trithionate with consequent formation of sulphate and liberation of sulphur dioxide. It is certain, however, that the main reaction is that which yields trithionate. With double thiosulphates, it is easier to demonstrate that trithionate is formed, and Spring (*Bull. Acad. roy. Belg.*, 1874, **37**, 45; *op. cit.*, Vol. 2, p. 966) showed that solutions of the double thiosulphates of an alkali metal and silver, mercury, or lead yield on boiling silver, mercury, or lead sulphide and alkali trithionate. Conversely, lead sulphide on digestion with potassium trithionate was converted into lead thiosulphate. When boiled with less than the equivalent amount of alkali, lead thiosulphate is largely converted into trithionate [Expt. I, (vii)], and also when boiled with dilute acetic acid [Expt. I, (viii)]. We find that weakly alkaline solutions of sodium thiosulphate on boiling yield sulphide and trithionate, but only a trace of sulphate. If they are boiled with sodium plumbite, lead sulphide is precipitated and trithionate remains in solution, which is in agreement with Spring's results (Expt. I).

With strongly alkaline solutions of thiosulphate, the above reaction would not be expected to occur to any extent, for, in the equilibrium (IX), increased alkalinity favours the formation of thiosulphate. A minute trace of sulphide always seems to be formed, however [Expt. I, (iii)].

Since trithionate on hydrolysis can yield sulphate, sulphite, and thiosulphate (pp. 1421, 1422), and thiosulphate yields trithionate, it follows that there are relationships, although indirect ones, between thiosulphate, sulphide, and sulphite on the one hand, and thiosulphate, sulphide, and sulphate on the other. The position can be seen from a consideration of the reactions

$$\begin{aligned}&2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6 \overset{H_2O}{\rightleftharpoons} 2H_2S + H_2S_2O_7 \overset{H_2O}{\rightleftharpoons} \\ &\qquad\qquad\qquad 2H_2S + 2H_2SO_4 \quad . \quad . \quad . \quad . \quad . \qquad \text{(i)}\end{aligned}$$

$$\left.\begin{aligned}&2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6 \\ &2H_2S_3O_6 \overset{H_2O}{\rightleftharpoons} H_2S_2O_3 + 4H_2SO_3\end{aligned}\right\} 3H_2S_2O_3 \overset{3H_2O}{\rightleftharpoons} 2H_2S + 4H_2SO_3 \, . \qquad \text{(ii)}$$

From (i) it is seen that in alkaline solution the equilibria of its constituent reactions lie right over to the left as regards the change of thiosulphate into sulphide and trithionate, and completely to the right as regards the hydration of pyrosulphuric acid. For this reason, both ends of the reaction chain (i) appear equally stable in alkaline solution. Only in very strong sulphuric acid solution is any change in the direction of trithionate and thiosulphate possible.

Conditions are somewhat similar as regards (ii). In alkaline solution, the positions of equilibria are well to the left as regards the thiosulphate–trithionate reaction, and well to the right as regards the conversion of trithionate into sulphite and thiosulphate (which occurs in the steps discussed on p. 1447), so that here also it is found that thiosulphate shows no tendency to be hydrolysed to sulphide and sulphite, whilst, on the other hand, sulphide and sulphite will not react to yield thiosulphate [Expt. I, (iv) and (v)].

If only the summation equations $H_2S_2O_3 + H_2O \longrightarrow H_2S + H_2SO_4$ and $3H_2S_2O_3 + 3H_2O \longrightarrow 2H_2S + 4H_2SO_3$ are considered, quite erroneous ideas are formed.

Foerster and Mommsen (*Ber.*, 1924, **57**, 258; see also Foerster and Vogel, *loc. cit.*, p. 168) found that sodium hydrogen sulphide and bisulphite react smoothly to yield sodium thiosulphate: $2NaHS + 4NaHSO_3 \longrightarrow 3Na_2S_2O_3 + 3H_2O$. This summation equation has the same form as (ii) above, but it would seem that it represents a mechanism entirely different from that considered above. In all probability, Foerster and Mommsen's synthesis of thiosulphate involved reactions (II*b*), (I*b*), and (VIII*b*), occurring in succession. Here again, since alkali strongly favours thiosulphate in reaction (VIII) and the mixture of sulphide and sulphite in reaction (ii), we have the curious position that in alkaline solution both thiosulphate and also the mixture of sulphide and sulphite are equally stable. Only in the neighbourhood of the neutral point is synthesis of thiosulphate possible by this method. We have found that sulphide and sulphite do not react in alkaline solution [Expt. I, (iv) and (v)].

Barium thiosulphate decomposes very slowly when boiled with water. Considerable quantities of polythionates are formed, but relatively little sulphate. The formation of barium sulphate equivalent to the barium thiosulphate would be expected if thiosulphuric acid decomposed according to the scheme $H_2S_2O_3 + H_2O \longrightarrow H_2SO_4 + H_2S$, in which case, moreover, the decomposition should be greatly accelerated by the presence of barium, as it is by the presence of salts of copper, silver, and mercury, even after allowance has been made for the fact that barium sulphate is not nearly so insoluble as the sulphides of these metals.

An experiment due to Muck (*Ber.*, 1871, **4**, 446) seems at first sight to show that direct action of hydrogen sulphide on sulphuric acid *is* possible. This author found that, on boiling manganese sulphide with a solution of ammonium sulphate, ammonia and hydrogen sulphide were expelled and trithionate was formed, although only in small amount. He gives no indication of the amount of trithionate formed and does not prove that it was not thiosulphate. It is clear that in this experiment the manganese sulphide serves merely as a source of hydrogen sulphide, which is liberated by the action of the acid produced from the ammonium salt by hydrolysis. We have repeated the experiment and find that it is thiosulphate which is produced, not trithionate. The amount formed is exceedingly small if one takes precautions to exclude air as thoroughly as possible. It is not easy to prevent the formation of a small amount of black oxide of manganese—a sure sign of oxidation—and the thiosulphate is probably formed by atmospheric oxidation of hydrogen, or possibly ammonium, sulphide, this oxidation being perhaps catalysed by the manganese oxide. It is known that atmospheric oxidation of ammonium sulphide solutions does give rise to thiosulphate. We found that an old ammonium sulphide solution, which had deposited sulphur and lost its colour, had become a strong solution of ammonium thiosulphate (Expt. J).

Hydrogen sulphide and strong sulphuric acid interact, especially when hot, to produce sulphur and sulphurous acid, and this is generally represented by means of the equation $H_2S + H_2SO_4 \longrightarrow H_2SO_3 + H_2O + S$. At the ordinary temperature, the sulphuric acid has to be almost $25N$ before any separation of sulphur occurs on passage of hydrogen sulphide. One would have expected interaction at lower concentrations if non-ionised sulphuric acid were the active agent in the oxidation. It seems much more likely that it is pyrosulphuric acid which reacts with the hydrogen sulphide in the first instance, and that the oxidation of the hydrogen sulphide by strong sulphuric acid takes place in several steps, the first of which consists in the formation of trithionic acid according to the equation

$$H_2S_2O_7 + H_2S \rightleftharpoons H_2S_3O_6 + H_2O \quad . \quad . \quad . \quad (XI)$$

It is probable that pyrosulphuric acid is present to some extent in acid as concentrated as 25*N*, but it is scarcely likely to be present at much lower concentrations.

Hydrolysis of the trithionic acid in the manner discussed on p. 1447 could yield sulphurous acid and thiosulphate, which would itself give sulphurous acid and sulphur. Sulphur could also be formed by interaction of hydrogen sulphide and the intermediate products of the hydrolysis. We consider that we have obtained small quantities of trithionic acid by the action of hydrogen sulphide on sulphuric acid of such a strength that sulphur is just not deposited when a current of hydrogen sulphide is passed through (Expt. K).

Trithionic acid must be regarded as being thiopyrosulphuric acid, and the hydrolysis of heavy-metal trithionates would yield pyrosulphuric acid in the first instance, and not two mols. of sulphuric acid as shown on p. 1418. On the above basis, the remarkable stability of thiosulphate towards alkali becomes intelligible,

Since an equilibrium $H_2S_2O_3 + H_2O \rightleftharpoons H_2S + H_2SO_4$ does not occur in any circumstances, there is no tendency for thiosulphate to be decomposed in such a manner by alkali, and likewise no possibility of interaction of sulphide and sulphate.

It is to be noted that in the equilibrium (IX) thiosulphuric and trithionic acids are of approximately the same strength, whilst hydrogen sulphide is much weaker. Alkali therefore shifts this equilibrium in favour of thiosulphate, and it is only in feebly alkaline solutions that there is any appreciable decomposition into sulphide and trithionate. Under more alkaline conditions, sulphide and trithionate readily yield thiosulphate, which is thus very stable in presence of strong alkali.

There is a difficulty in connexion with the hydrolysis of trithionates which has been pointed out by Foerster and Hornig (*Z. anorg. Chem.*, 1922, **125**, 119). Both in weakly alkaline and in weakly acid solutions, the hydrolysis of trithionic acid follows a course which can be represented by the equation $H_2S_3O_6 + H_2O \longrightarrow H_2SO_4 + H_2S_2O_3$. This hydrolysis is enormously accelerated by salts of copper, silver, and mercury with precipitation of the sulphides of these metals. This would be explicable, if the above hydrolysis is reversible, by the disturbance of the equilibrium caused by decomposition of the thiosulphuric acid brought about by the insolubility of the metal sulphides precipitated. Against this view of the matter is the fact that the presence of added sulphate does not seem to slow down the rate of hydrolysis, whilst the presence of barium salts does not appreciably accelerate it, as might have been expected in view of the insolubility of barium sulphate.

The following is a possible way out of the difficulty : Trithionic acid is an equilibrium mixture of the two forms

$$(a)\ SH{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}OH \rightleftharpoons OH{\cdot}SO_2{\cdot}S{\cdot}SO_2{\cdot}OH\ (b)$$

both of which could equally well be formed from thiosulphuric acid by elimination of hydrogen sulphide; form (*b*) seems to be favoured by alkaline conditions, which would indicate that it is the more acidic of the two—possibly because of its greater symmetry. Under ordinary conditions of acidity both forms will be present, (*a*) predominating. Equilibrium between the two forms is probably established very rapidly. Hydrolysis of form (*a*) yields, in the first instance, hydrogen sulphide and pyrosulphuric acid, and it is not surprising that the hydrolysis is greatly accelerated by copper, silver, and mercury salts owing to the insolubility of the sulphides of these metals. There is, however, no reason why a barium salt should accelerate hydrolysis in this direction, for in the equilibria

$$H_2S_3O_6 + H_2O \rightleftharpoons H_2S + H_2S_2O_7 \overset{+H_2O}{\rightleftharpoons} H_2S + 2H_2SO_4$$

the pyrosulphuric acid would be hydrated nearly as quickly in absence of barium as in its presence, since the equilibrium would be almost entirely in favour of sulphuric acid except in very acid concentrated solutions. For a similar reason, sulphate ions have little influence on the rate of hydrolysis.

The results of Kurtenacker and Kaufmann (*Z. anorg. Chem.*, 1925, **148**, 43) and of Foerster and Hornig (*loc. cit.*, p. 86) show that under neutral and acid conditions and in absence of heavy metals the hydrolysis of trithionic acid yields chiefly sulphate and thiosulphate. In presence of sodium acetate, quantitative agreement with the equation $H_2S_3O_6 + H_2O \longrightarrow H_2SO_4 + H_2S_2O_3$ is obtained (Foerster, *ibid.*, 1925, **144**, 337). It does not necessarily follow, however, that this is the primary reaction.

Kurtenacker and Kaufmann (*loc. cit.*, p. 369) have shown that in strongly alkaline solutions the hydrolysis of trithionate yields no sulphate, but only sulphite and thiosulphate: $2H_2S_3O_6 + 3H_2O \longrightarrow H_2S_2O_3 + 4H_2SO_3$. We consider the possible mechanism of this change on p. 1447. With decreasing alkalinity, sulphate is formed as well as sulphite and thiosulphate. In presence of sodium acetate, *i.e.*, under practically neutral conditions, sulphate and thiosulphate are formed in equimolecular proportion, as Foerster showed. Rapid hydrolysis of trithionate in strongly acid solution yields more than one-third of the original sulphur in the form of sulphate. This agrees with the views expressed above, but does not prove that they are correct, for the extra sulphate might possibly be derived from polythionates formed by the Wackenroder reaction from hydrogen sulphide and sulphur dioxide, which are also formed during the hydrolysis. We do not think this is very likely, however (Expt. L).

We believe that trithionate never yields sulphate and thiosulphate directly on hydrolysis (which is why neither barium nor sulphate ions influence the reaction appreciably). Form (*a*) yields hydrogen sulphide and pyrosulphuric acid only, in the first instance, whilst form (*b*) is hydrolysed in the manner discussed on p. 1447. This in three steps leads to the reaction actually realised in strongly alkaline solution: $2H_2S_3O_6 + 3H_2O \longrightarrow H_2S_2O_3 + 4H_2SO_3$. Now sulphoxylic acid is an intermediate product in the hydrolysis of the (*b*) form, and would react with hydrogen sulphide formed on hydrolysis of form (*a*). If forms (*a*) and (*b*) were present in equal proportion and hydrolysed at the same rates, we should have the following combinations of reactions :

$$\begin{array}{rl}
\text{(Two steps) } H_2S_3O_6 + 2H_2O & \rightleftarrows 2H_2SO_4 + H_2S \\
\text{(Two steps) } H_2S_3O_6 + 2H_2O & \rightleftarrows 2H_2SO_3 + (HO)_2S \\
H_2S + (HO)_2S & \rightleftarrows 2S + 2H_2O \\
2H_2SO_3 + 2S & \rightleftarrows 2H_2S_2O_3
\end{array}$$

$$2[H_2S_3O_6 + H_2O \rightleftarrows H_2SO_4 + H_2S_2O_3]$$

This balanced state of the two modes of hydrolysis seems to occur in neutral solution.

It is noteworthy in connexion with the above suggestions that hydrogen sulphide is always formed during the acid hydrolysis of trithionate, as was noticed by Kessler (*Pogg. Ann.*, 1848, **74**, 262). The fact that it is noticeable more particularly at the very commencement of the action suggests that it is, in the main, a real primary product rather than a product of decomposition of the thiosulphate.

Needless to say, and as Foerster and Hornig and Kurtenacker and Kaufmann have shown, the other polythionic acids are formed during the acid hydrolysis of trithionate as in all acid decompositions of sulphur acids, but these are due to later changes than those now being discussed. In Expt. M we record two hydrolytic experiments which extend Kurtenacker and Kaufmann's results.

Reaction (VIII).—Under most conditions, reaction (VIII) occurs to the largest extent. It involves a perfectly definite equilibrium, such that in alkaline solution the thiosulphate is very stable. On this account, thiosulphate is readily formed by boiling alkaline sulphite solutions with sulphur. Nevertheless, even in the alkaline solutions there may be a perfectly definite although very small dissociation into sulphite and sulphur. If alkaline thiosulphate solutions containing alkali sulphide are boiled in absence of air, they become deep yellow owing to formation of polysulphide, the extra sulphur for which is obtained from the thiosulphate. A similar result is obtained by boiling an alkaline thiosulphate solution with sodium formaldehydesulphoxylate. The yellow solution obtained gives an immediate precipitate of lead sulphide with lead plumbite. This is rather an elegant method of showing that sulphide is formed on alkaline hydrolysis of sulphoxylate (compare p. 1403).

The equilibrium between sulphide and thiosulphate may be written $Na_2S + Na_2S_2O_3 \rightleftarrows Na_2S_2 + Na_2SO_3$, although higher polysulphides might result as well. Such a reaction does not necessarily involve any dissociation of thiosulphates into sulphite and sulphur. There can be little doubt that it is because of such equilibria that a trace of hydrogen sulphide greatly accelerates the reaction between sodium sulphite and sulphur. We have found that sometimes there is a long delay before sulphur begins to dissolve in boiling sodium sulphite solution, and in such cases the effect of passing a few bubbles of hydrogen sulphide into the solution is very marked; once the reaction has commenced it proceeds smoothly. The catalytic action of sulphide has been referred to recently by Watson and Rajagopalan (*J. Indian Inst. Sci.*, 1925, **8**, A, 275), and had been previously noted by Hargreaves and Dunningham (*J. Soc. Chem. Ind.*, 1923, **42**, 147T). Alkali also catalyses the reaction owing to the production of sulphide by hydrolysis of the sulphur. It must be supposed that sodium sulphide or hydrogen sulphide is more efficient in detaching atoms of sulphur from solid sulphur than is sodium sulphite.

Holleman (*Rec. trav. chim.*, 1895, **14**, 71) considered that the decomposition of thiosulphuric acid into sulphur and sulphurous acid followed a unimolecular course, although he recognised that the figures with which he supported this view indicated some complication. He does not seem to have considered the possibility of a bimolecular reaction, although his figures give better values for such a reaction.

His method was to determine by an iodine titration the amount of decomposition which had occurred in sodium thiosulphate solutions of different concentrations one minute after mixing with the equivalent amount of hydrochloric acid. His three experiments are given below, with the values of k calculated for uni- and bimolecular reactions.

Mixture used.	k_{uni}.	k_{bi}.
M-$Na_2S_2O_3$ added to $2M$-HCl	0·437	1·124
$M/2$-$Na_2S_2O_3$ added to M-HCl	0·258	1·209
$M/5$-$Na_2S_2O_3$ added to $2M/5$-HCl	0·068	0·717

The correct values for k cannot be calculated from Holleman's data. He assumed, erroneously, that when decomposition was complete the final value of the iodine titre would be twice the initial titre, and on this basis he calculated the concentration of thiosulphate left after one minute. The true values are less than those used in the above calculations, for, owing to polythionate formation, thiosulphate disappears more quickly than is indicated by the increase in the iodine titre. We find that, instead of increasing to double the original titre, the final titre may be only 20—80% greater.

As it is now generally accepted that unimolecular reactions are very uncommon (see, *e.g.*, Hinshelwood and Topley, J., 1924, **125**, 393), we have examined the kinetics of the decomposition of thiosulphuric acid more fully. The method used was to titrate acidified solutions after different intervals of time with standard iodine solution, continuing until the iodine titre reached a maximum value and became approximately constant or even decreased.

It is evident from the figures quoted (Expt. N) that the maximum value of the iodine titre is smallest for the most dilute solutions, and tends to increase both with increasing concentration of thiosulphate and with increasing acidity. Even in the most acid solution examined, the maximum titre was only 75% greater than the initial. If thiosulphuric acid decomposed only according to reaction (VIII), the iodine titre would eventually become doubled; if the decomposition was entirely according to reaction (IX), the titre would remain unaltered. If both modes of decomposition occur together, then reactions (II*b*) and (I*b*) follow as a matter of course, and, provided reactions (VIII) and (IX) occur in the right proportion, the iodine titre might fall to zero.

The greater part of the sulphurous acid formed in reaction (VIII) becomes either pyrosulphurous acid or sulphur dioxide and, when extended to include these changes, reaction (VIII) corresponds to a greater decrease of acidity than does reaction (IX). It follows that the more acid the conditions under which thiosulphuric acid decomposes, the more may reaction (VIII) be expected to predominate as compared with reaction (IX) (compare pp. 1430—31). The increase in the maximum iodine titration with increasing acidity, in the experiments under consideration, seems to be mainly due to such an increase in the relative importance of reaction (VIII).

The reason for the existence of a maximum iodine titre at all must be considered. From the experiments quoted, it will be seen that it is practically only in the cases where acid and thiosulphate are mixed in equivalent amounts that well-marked maxima exist. Moreover, in these cases the maxima occur at a very early stage of the reaction. In experiments where excess of acid was used, the iodine titre slowly approached a limiting value, and if it subsequently diminished at all it did so very slowly. In those cases where thiosulphate and acid were mixed in equivalent amounts, the acidity of the mixed solution at the commencement may be considered as being due entirely to thiosulphuric acid, which is a strong acid. As decomposition proceeds, according to reactions (VIII) and (IX), supplemented by reactions (II*b*) and (I*b*), a considerable decrease of acidity occurs. Because of this diminution in the acidity of the solution, reaction (IX) tends to increase relatively to reaction (VIII) as the decomposition proceeds, and this could account for the experimentally observed maximum iodine titre, for not only does reaction (IX) itself cause no increase in the original titre, but, in consequence of reactions (II*b*) and (I*b*), it will lead to the destruction of some of the accumulated sulphurous acid and so cause a decrease in the iodine titre.

Even in very weakly acid solutions, reactions (II*b*) and (I*b*) in conjunction seem to occur with great rapidity owing to the considerable decrease in acidity which they produce, and in all but the weakest and least acid solutions we may safely assume that none of the iodine reduction is due to either hydrogen sulphide or sulphoxylic acid. It is because of the rapidity of these reactions that hydrogen sulphide cannot be detected by means of lead salts (Holleman, *loc. cit.*) or even silver salts in acidified thiosulphate solutions, but it can, in favourable circumstances (Expt. H), be detected in the vapours given off from such solutions on boiling, owing to the fact that hydrogen sulphide and sulphur dioxide can coexist in presence of water vapour and need liquid water for interaction to occur (Matthews, *loc. cit.*).

It will be found that the combination of reactions (VIII) and (IX) with (II*b*) and (I*b*)* just sufficient to remove all the hydrogen sulphide formed by reaction (IX) yields the summation equation

$$10H_2S_2O_3 \longrightarrow 4H_2S_3O_6 + 4S_2 + 6H_2O,$$

8 mols. of thiosulphuric acid having decomposed according to reaction (IX), and 2 mols. according to reaction (VIII). Now it is clear that, for any increase at all to occur in the iodine titre of the

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* Bearing in mind that $H_2S_2O_5$ is formed from $2H_2SO_3$ by loss of water, whilst HO·S·O·S·OH yields $2S(OH)_2$ by addition of water.

decomposing thiosulphate solution, an additional 10 mols., at least, of thiosulphuric acid must decompose according to reaction (VIII) in the early stages of the decomposition. The 20 mols. of thiosulphuric acid would require 20 atoms of iodine for oxidation to tetrathionate. If, however, 10 decomposed as in the above equation, the products would not react with iodine, but the 10 mols. of sulphurous acid formed by the remaining 10 mols. of thiosulphuric acid would require 20 atoms of iodine for oxidation to sulphate. It would appear that in all the cases we have studied, more than 50% of the decomposition took place in accordance with reaction (VIII), and usually a much larger proportion.

It is evident that if the sulphoxylic acid formed by reaction (II*b*) did persist at all, it would have a large effect on the iodine titre, since 1 mol. of sulphoxylic acid requires 4 atoms of iodine to oxidise it to sulphuric acid. It would be possible for a maximum in the iodine titre to arise, quite apart from any change in the relative proportions in which reactions (VIII) and (IX) took place, from an accumulation of sulphoxylic acid in the early stages of the decomposition of thiosulphuric acid, followed by its destruction by interaction with hydrogen sulphide at a later stage. This is unlikely to occur except in dilute and weakly acid solutions, but we have satisfied ourselves that even in solution (*c*) (see Table V) no sulphoxylic acid can be detected. This solution was found to behave exactly like thiosulphate towards methylene-blue (see p. 1435), whilst with ammoniacal silver nitrate it gave no metallic silver, as would sulphoxylic acid, but after many hours' standing it gave an amount of silver sulphide which more or less corresponded to the thiosulphate left undecomposed at the moment of adding the ammoniacal silver nitrate.

During the early stages of the decomposition of thiosulphuric acid, a certain proportion of tetra- and penta-thionic acids will have been formed in many cases owing to reactions (XIV*a*) and (XV*a*)—and perhaps (XII*a*) and (XIII*a*). Towards the end of the decomposition, the higher polythionates will have become less stable owing to the general decrease of acidity (see p. 1448), and reactions (XIV*b*) and (XV*b*) will tend to take place. Decomposition of the thiosulphuric acid so produced would occur in accordance with reaction (IX), whilst the hydrogen sulphide formed would cause further destruction of sulphurous acid. It is probable that some of the very slow decrease in the iodine titre at the end of the decomposition is to be accounted for in this way.

Moreover, from the fact that more sulphate was formed in the latest stages of the (*b*) experiment (see Table V) than corresponds to the iodine titration, it would seem that slow hydrolysis of trithionate under the influence of sulphurous acid sets in after an hour or less.

It is evident from the preceding discussion that, in those cases where a well-marked maximum occurs, decomposition of the thiosulphate will probably not be complete when this maximum is reached. The amount of thiosulphate still undecomposed is readily obtained by determining the sulphate present after the iodine titration, assuming that sulphurous and thiosulphuric acids had been the only substances present which reacted with iodine. This determination was made in a number of cases, the titrated solution being heated just to boiling immediately before adding the barium chloride. No appreciable hydrolysis of polythionates occurs under these conditions. The amounts of thiosulphate decomposed at earlier stages [x in the fourth columns of Table V, (*a*), (*b*), and (*c*)] were calculated from the values so found for the maxima, on the assumption that they were proportional to the iodine titre. Using these figures, the bimolecular velocity coefficients were calculated and surprisingly good values were obtained.

In the case of experiments (*a*) and (*b*), the sulphate estimation was made in each case after the iodine titration. The tables show that the rate of decomposition of thiosulphate, under the conditions of these experiments, increases very rapidly with increase in concentration of thiosulphate. In the very early stages of the decomposition the amount transformed in a given time is roughly proportional to the *square* of the thiosulphate concentrations, whilst the time taken to complete a certain fraction of the decomposition is, to a rough approximation, inversely proportional to the initial concentration of thiosulphate.

In those experiments where excess of hydrochloric acid was used, the influence of thiosulphate concentration was of the character just stated for a considerable proportion of the reaction, but where acid and thiosulphate were used in equivalent amounts, the figures show that during most of the decomposition the weaker solutions were decomposing at a greater rate than would be expected from the concentration, and this becomes more obvious as the decomposition proceeds.

It is probable that as reaction (IX) increases relatively to reaction (VIII) in the dilute, weakly acid solutions, the increased extent to which reactions (II*b*) and (I*b*) occur will have an appreciable accelerating effect on both reactions (VIII) and (IX), so that, as a whole, the decomposition of thiosulphate proceeds at a relatively enhanced rate.

When all the results summarised in Expt. N and discussed above are considered critically, they indicate that the decomposition of thiosulphuric acid follows a bimolecular course over a considerable range. Some caution must, of course, be used in interpreting the results of reaction-velocity determinations with such complex systems as that under discussion.

It is admitted that the decomposition of thiosulphuric acid is a mixed reaction and due to two simultaneous primary changes (VIII) and (IX), but as, under the conditions studied, the change into sulphurous acid and sulphur represented 50—75% of the whole decomposition, such good agreement with the bimolecular formula could scarcely be obtained unless this change were bimolecular. In fact, the results support the view that both primary reactions are bimolecular. Reaction (VIII) must therefore be represented by the equation $2H_2S_2O_3 \rightleftharpoons 2H_2SO_3 + S_2$. This seems to show that the sulphur unit concerned (we hesitate to call it a molecule) is S_2, and may explain why hydrogen sulphide catalyses the reaction between sodium sulphite and solid sulphur. Since hydrogen sulphide can combine with S_2 to form hydrogen trisulphide, whilst sodium sulphite can only combine with one atom of sulphur, 1 mol. of hydrogen sulphide could detach the S_2 unit from solid sulphur, whereas 2 mols. of sodium sulphite would have to co-operate. Since hydrogen disulphide also exists, the trisulphide could pass on its extra sulphur to sodium sulphite in two steps :

$$\left\{\begin{array}{l} H_2S_3 + Na_2SO_3 \rightleftharpoons Na_2S_2O_3 + H_2S_2 \\ H_2S_2 + Na_2SO_3 \rightleftharpoons Na_2S_2O_3 + H_2S. \end{array}\right.$$

It may be pointed out that our reaction (I) for the hydrolysis of sulphur suggests that sulphur acts as though composed of S_2 units.

The $\left[\begin{matrix} O & & O \\ & S & \\ O & & S \end{matrix}\right]''$ ion of the thiosulphates is very stable, having a very small tendency to drop the second sulphur atom and become $\left[\begin{matrix} O & & O \\ & S & \\ O & & \end{matrix}\right]''$. In dilute solutions of thiosulphuric acid which do not contain another acid, this should still be true. It is probably not until the hydrogen ions become attached to the S_2O_3'' ion by covalencies instead of electrovalencies that rapid decomposition of thiosulphuric acid begins. This occurs the more readily the greater the thiosulphate and hydrogen-ion concentrations. Dilute acid solutions should therefore contain unaltered thiosulphuric acid and its ions for some time. Now one of the most marked characteristics of the S_2O_3'' ion is that it can be readily oxidised to the S_4O_6'' ion. The great majority of oxidising agents which are not too violent actually oxidise thiosulphate to tetrathionate, but it is not commonly realised what a powerful reducing agent thiosulphate is. Spring [*Bull. Acad. roy. Belg.*, 1881, (iii), **1**, 106; *op. cit.*, Vol. II, p. 1109] found that freshly acidified solutions of thiosulphate bleached indigo, and he attributed this to the presence of hydrosulphurous acid. There can be little doubt, however, that the bleaching is due to thiosulphuric acid, for we find that under suitable conditions either weakly or strongly acidified solutions of thiosulphate can be titrated quantitatively to tetrathionate, either with indigo or, much more conveniently, with methylene-blue. The reaction is bimolecular and is greatly accelerated by hydrogen ions. Litmus and methyl-orange are also reduced by the acidified thiosulphate solutions.

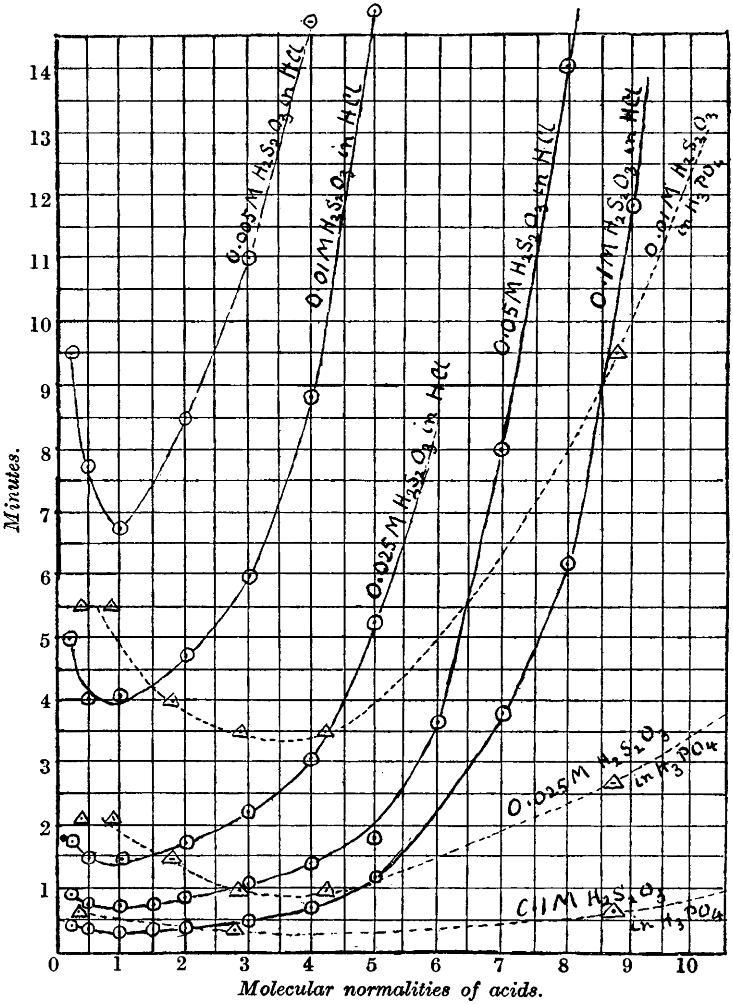
Gil and Beato (*Anal. Fís. Quím.*, 1924, **22**, 84) found that if sodium thiosulphate was added to concentrated hydrochloric acid, pure sodium chloride was precipitated, whilst the separated solution remained perfectly clear, without any deposition of sulphur, for many hours. They concluded that thiosulphuric acid became more stable the greater the acidity of the solution. This view in its simple form is contrary both to experience and to the principle of Le Chatelier. Were it true, then thiosulphate would become less stable in alkaline solution, which is not the case, whilst there can be no question that at low acidities thiosulphate decomposes the more quickly the greater the acidity.

The non-appearance of sulphur does not show that no decomposition of thiosulphuric acid has occurred. Holleman (*loc. cit.*) showed that decomposition began as soon as thiosulphuric acid was liberated from its salts, even although no sulphur had separated. He considered that this was due to the sulphur liberated by reaction (VIII) remaining in colloidal solution, because an acidified thiosulphate solution, if neutralised before the time when separation of sulphur occurred normally, still deposited sulphur. On repeating his experiments, we confirmed these results, but we did not observe this separation of sulphur on neutralisation in all circumstances if the thiosulphate solutions were much weaker than those used by Holleman (see p. 1433).

When the time taken for the sulphur to become visible (compare Gaillard, *Compt. rend.*, 1905, **140**, 652; Oettingen, *Z. physikal. Chem.*, 1900, **33**, 1) is noted for solutions of increasing acidity, it is found to pass through a minimum, and with very high acidities no sulphur separates until after many hours, as in Gil and Beato's experiment. The minimum occurs in solutions which are approximately *N* in hydrogen-ion concentration, no matter what the thiosulphate concentration, as is well shown in Fig. 1; phosphoric acid has a similar effect to hydrochloric acid when allowance is made for its much lower hydrogen-ion concentration (Expt. O).

The delay in the separation of sulphur at high acidities is easily explained on the basis of our theory of the decomposition of thiosulphuric acid. It is not due to strong hydrochloric acid retarding the change $HS_2O_3' \longrightarrow HSO_3' + S$, as supposed by Foerster and Vogel (*loc. cit.*, p. 183). Both reactions (VIII) and (IX) are accelerated by acid, the former more so than the latter, owing to the fact that the greater part of the sulphurous acid becomes sulphur dioxide. Reaction (VIII), when extended to include the formation of sulphur

FIG. 1.



Times of appearance of sulphur in acidified thiosulphate solutions.
All normalities to be multiplied by $\frac{10}{11}$ to obtain actual concentrations.

dioxide, corresponds to a greater decrease of acidity than does reaction (IX), hence the preferential influence of hydrogen ions on (VIII). The experiments we have already quoted (Expt. N) bear out the correctness of this deduction.

The simultaneous occurrence of reactions (VIII) and (IX) brings in reactions (II*b*) and (I*b*) which are also favoured by acid. Tetra- and penta-thionic acids are formed from trithionic acid either by direct addition of sulphur,

$$H_2S_3O_6 + S \rightleftharpoons H_2S_4O_6\ (2H_2S_3O_6 + S_2 \rightleftharpoons 2H_2S_4O_6) \quad . \quad . \quad (XII)$$

$$H_2S_4O_6 + S \rightleftharpoons H_2S_5O_6\ (2H_2S_4O_6 + S_2 \rightleftharpoons 2H_2S_5O_6) \quad . \quad . \quad (XIII)$$

or by interaction with thiosulphuric acid,

$$H_2S_3O_6 + H_2S_2O_3 \rightleftharpoons H_2S_4O_6 + H_2SO_3 \quad . \quad . \quad . \quad (XIV)$$

$$H_2S_4O_6 + H_2S_2O_3 \rightleftharpoons H_2S_5O_6 + H_2SO_3 \quad . \quad . \quad . \quad (XV)$$

and all these reactions are favoured by acidity (see p. 1448). The occurrence of these last four reactions represents, in the aggregate, a large decrease of hydrogen-ion concentration and so is greatly favoured by acidity. The more they occur the less the extent to which reaction (VIII*a*) can occur, but this effect on the decomposition of thiosulphuric acid as a whole does not become apparent until a reasonable amount of trithionic acid has been formed by reaction (IX).

That the effect is real is readily shown by acidifying under similar conditions pure thiosulphate or a mixture of thiosulphate with tri- or tetra-thionate. The mixtures take much longer than the pure thiosulphate to give a deposit of sulphur (Expt. P).

We are inclined to think that reactions (XIV) and (XV) are much more important than reactions (XII) and (XIII) for building up the polythionates. We could obtain no certain proof that colloidal sulphur, prepared by Svedberg's method (*Z. Chem. Ind. Koll.*, 1909, **4**, 49), was absorbed at all by trithionic acid, but sulphur liberated in presence of trithionic acid, by the interaction of hydrogen sulphide and iodine, was readily taken up to form tetrathionate. No satisfactory conversion of tetrathionate into pentathionate could be obtained by this method (Expt. Q). A solution of sulphur in benzene seemed to have no action on either trithionate or tetrathionate.

Increase in hydrogen-ion concentration thus tends, on the one hand, to diminish the time required for the separation of sulphur in so far as it accelerates reaction (VIII*a*), but, on the other hand, it lengthens the time required by favouring all the opposing reactions mentioned above. In such circumstances, the occurrence of a minimum time of appearance of sulphur at a fairly definite acidity is only to be expected.

All the reactions occurring in the acidified thiosulphate proceed with a diminution of acidity. They gradually become slower as the limiting concentrations of the several polythionic acids characteristic of the prevailing hydrogen-ion concentration are approached (see p. 1448). Since the hydrogen-ion concentration gradually diminishes, the system is never fully stable—readjustments are continually necessary which ultimately lead to the decomposition of the polythionic acids with separation of sulphur.

It is here appropriate to consider the marked influence of arsenious oxide in preventing separation of sulphur and promoting the formation of pentathionic acid from thiosulphate. This phenomenon was discovered by Salzer (*Ber.*, 1886, **19**, 1696) and has been applied by Raschig (*Z. angew. Chem.*, 1920, **33**, 260). It is known that sulphur oxidises arsenite to oxythioarsenate, and no doubt Salzer was right in thinking that the latter played an important part in the reaction. The oxythioarsenate would act in two ways. (1) Owing to its ready formation, it would prevent separation of sulphur from thiosulphuric acid by reaction (VIII). This would probably be due to the direct reaction $H_2S_2O_3 + H_3AsO_3 \rightleftarrows H_2SO_3 + H_3AsO_3S$ (assuming that H_3AsO_3S is the only oxythioarsenate involved). The oxythioarsenate would yield its sulphur to trithionic acid, formed in the normal way by reaction (IX), to give tetra- and penta-thionic acids in two stages: $H_2S_3O_6 + H_3AsO_3S \rightleftarrows H_2S_4O_6 + H_3AsO_3$, $H_2S_4O_6 + H_3AsO_3S \rightleftarrows H_2S_5O_6 + H_3AsO_3$. (2) It could also take up any sulphur found by reactions (II) and (I) and pass it on as above: $H_3AsO_3 + S \rightleftarrows H_3AsO_3S$ (or $2H_3AsO_3 + S_2 \rightleftarrows 2H_3AsO_3S$).

Under favourable conditions, complete conversion of thiosulphate into pentathionate is theoretically possible with the help of small quantities of arsenious oxide, and very good yields are actually obtainable. It will be observed that the arsenious acid is really a vehicle for the handing on of sulphur to trithionic acid just as is sulphurous acid, the oxythioarsenic acid playing the same rôle in the one case as thiosulphuric acid in the other. There is also a superficial resemblance between the action of arsenious acid and of strong hydrochloric acid in preventing separation of sulphur. The reasons for the two actions are different, however, although both depend on the introduction or acceleration of reactions which use up sulphur more quickly than it is produced by reaction (VIII).

If dilute thiosulphate solutions are treated with less acid than corresponds to the minima in the curves of Fig. 1 and then quickly neutralised before sulphur becomes visible, separation of sulphur may be entirely prevented if the addition of alkali has been made an appreciable time before precipitation would normally occur. If, however, the alkali is added very shortly before separation of sulphur would occur normally, its addition causes immediate separation of sulphur, and in such cases either alkali or lanthanum nitrate will produce a precipitate. Solutions to the right of the minima still give the reactions for colloidal sulphur with separation of sulphur on addition of alkali or lanthanum nitrate, but we believe that they also contain pentathionate (although this is difficult to prove), the proportion of pentathionate increasing with acidity and time and that of colloidal sulphur diminishing (Expt. R).

It is not possible to apply the neutralisation test to the very acidic mixtures, for if the whole amount of concentrated alkali needed for neutralisation is added suddenly, the heat liberated causes complications, whilst if neutralisation is effected slowly, one passes into the less acid regions, where sulphur separates rapidly. Neutralisation of such solutions is therefore incapable of throwing light on the conditions prevailing therein at the stage prior to separation of sulphur.

Reaction (X).—In the very acid solutions, not only is reaction (VIII) delayed, but so also is the formation of pentathionate, and in fact thiosulphuric acid seems to have become more stable, as Gil and Beato suggested. The peculiar facts can be satisfactorily accounted for in terms of a reaction

$$2H_2S_2O_3 \rightleftharpoons H_2O + H_2S_4O_5 \quad . \quad . \quad . \quad . \quad . \quad (X)$$

It is obvious that such a reaction is theoretically possible, and it is to be noted that it would be extremely effective as a means of removing hydrogen ions. It is reasonable, therefore, to suppose that it may occur in very acid solution, but it may well occur to some extent under much less acid conditions, although in such circumstances the active mass of water will usually be so great that it could not proceed very far. It may be noted in this connexion that we have found that a strong zinc chloride solution will greatly delay the separation of sulphur from acidified thiosulphate. In one experiment, sulphur appeared after 6 minutes when zinc chloride was used, but after 35 seconds when the zinc chloride solution was replaced by an equal volume of water. The effect of zinc chloride is thus quite marked, but, as it only depends on a dehydrating action, it is naturally much less than the effect produced by strong hydrochloric acid, which depends on a hydrogen-ion action as well.

There is no reason why $H_2S_4O_5$ should not be much more stable towards loss of sulphur or of hydrogen sulphide than is the simple thiosulphuric acid—in fact we think it likely that it would be. As regards the direct loss of sulphur, it might be argued that, if we are right in supposing that in the case of thiosulphuric acid this occurs in such a way as to eliminate an S_2 unit: $2H_2S_2O_3 \rightleftharpoons 2H_2SO_3 + S_2$, then it should occur still more readily from $H_2S_4O_5$, where the thiosulphate molecules have already been brought together. But when the known weakness of the second-stage ionisation of sulphurous acid is considered in conjunction with the known tendency for sulphur to become co-ordinated with four atoms or groups, there are good reasons for thinking that the direct loss of sulphur by thiosulphuric acid is largely due to the fact that a hydrogen atom is able to take the place of the escaping sulphur atom.

If this is correct, the decomposition of thiosulphuric acid according to reaction (VIII) is to be regarded as giving rise to sulphur and sulphonic acid, not sulphurous acid :

$$2H_2\left[\begin{smallmatrix}O & & O\\ & S & \\ O & & S\end{smallmatrix}\right] \rightleftarrows 2H\left[\begin{smallmatrix}O & & O\\ & S & \\ O & & H\end{smallmatrix}\right] + S_2.$$

This would be another reason for the great stability of the alkali-metal thiosulphates in neutral or alkaline solution, for the alkali-metal atoms cannot become co-ordinated in the same way as a hydrogen atom—their valencies are always electrovalencies.

In view of the fact that $H_2S_2O_5$, pyrosulphurous acid, is a strong acid, there would not be the same possibility of hydrogen taking the place of sulphur in the manner just indicated were $H_2S_4O_5$ to shed an S_2 unit. $H_2S_4O_5$ may therefore be expected to be very stable towards direct loss of sulphur, but in other directions it would react very much like thiosulphuric acid. This appears to be the case in its behaviour towards oxidising agents. Thiosulphate solutions which have been treated with a large excess of concentrated hydrochloric acid (Gil and Beato's solution) still reduce iodine. Titration with iodine at known intervals of time, in conjunction with subsequent determination of the sulphate present in the oxidised solution, has shown that thiosulphate (actually $H_2S_4O_5$, according to us) persists for a surprising length of time—much longer than in the case of less strongly acidified solutions (compare Expt. N). Even after 2 hours nearly 30% remained undecomposed (Expt. S).

The strongly acid thiosulphate solutions also exert a strong bleaching action on indigo, methylene-blue, litmus, and methyl-orange, and we find that they can be titrated smoothly and rapidly with methylene-blue (indigo can be used, but is not so satisfactory, as it reacts more slowly).

The amount of methylene-blue which is bleached is in close agreement with that required by the reaction

$$\underset{\text{(methylene-blue)}}{C_{16}H_{18}N_3SCl} + H_2S_4O_5 + H_2O = \underset{\text{(\textit{leuco}-methylene-blue)}}{C_{16}H_{19}N_3S} + H_2S_4O_6 + HCl,$$

or more probably (see Expt. T)

$$C_{16}H_{18}N_3SCl + S_4O_5'' + H_2O = C_{16}H_{19}N_3S,HCl + S_4O_6''.$$

The rate at which the methylene-blue is bleached is very greatly increased by rise of temperature. The strongly acidic bleached solutions are comparatively stable towards atmospheric oxidation, but the blue colour is at once restored by a drop or two of strong nitric acid, by hydrogen peroxide, or even by silver nitrate or silver acetate. This behaviour towards silver has prevented us from carrying out any direct estimation of the tetrathionate formed in the reaction between thiosulphate and methylene-blue. We have, however, isolated the *leuco*-methylene-blue formed in the reaction (Expt. T).

The only alternative explanation of the quantitative relationships between methylene-blue and thiosulphate found experimentally would seem to be that a colourless addition compound is formed between one molecule of methylene-blue and one of $H_2S_4O_5$ (or two molecules of $H_2S_2O_3$). Such an explanation appears to be completely ruled out by the fact that the bleached solutions remain colourless under the following treatments: (1) Dilution with air-free water; (2) boiling in absence of air; (3) cautious treatment with hydrogen sulphide or sulphur dioxide, which react with and destroy thiosulphate; (4) addition of formaldehyde, which forms trithioformaldehyde with thiosulphuric acid; or (5) long boiling with $5N$-hydrochloric acid in absence of air—a complex containing thiosulphuric acid could scarcely remain undecomposed by such treatment. Lastly, it may be mentioned that the action of methylene-blue in preventing the separation of sulphur, which is dealt with in the next paragraph, would be difficult to account for on any other basis than tetrathionate formation.

Even in comparatively weakly acid solutions (of N-hydrogen-ion concentration, or even less) thiosulphate can be titrated with methylene-blue, apparently with the same end results as in very acid solutions. If the methylene-blue is added as fast as it is decolorised, no separation of sulphur occurs. This is owing to conversion of tetrathionate into pentathionate according to reaction (XV*a*) (compare Expt. P); but as thiosulphate is oxidised to tetrathionate, more is formed from pentathionate by reaction (XV*b*). As a consequence of this, almost complete conversion of thiosulphate into tetrathionate by methylene-blue is possible if sufficient time is taken and sulphur dioxide is not allowed to escape. Whether, in such weakly acid solutions, the reaction involves $H_2S_4O_5$ must remain undecided. It may occur in two steps, first the formation of an addition compound $H_2S_2O_3$–methylene-blue, and then the interaction of this with a second molecule of thiosulphuric acid.

It is very probable that the reaction between thiosulphate and iodine is of this character and actually bimolecular. It is generally represented as being termolecular :

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2HI \text{ (or } 2S_2O_3'' + I_2 \longrightarrow S_4O_6'' + 2I'\text{)}.$$

In view of the rapidity with which it occurs, it cannot really be termolecular, but it could well occur in two stages, the first involving formation of $Na_2S_2O_3,I_2$ or S_2O_3,I_2'', and the second the reaction of this compound with a second thiosulphate molecule or ion. The iodine and methylene-blue would probably become attached to the outer sulphur atom of the S_2O_3 group, just as sulphur dioxide does in the yellow compounds, $Rb_2S_2O_3,SO_2$, etc.

Some determinations of the time required to bleach a constant amount of methylene-blue with varying concentrations of sodium thiosulphate, taken in excess, and of hydrochloric acid are in agreement with what we consider to be the mechanism of the reduction (Expt. U).

It is likely that the $H_2S_4O_5$ (or S_4O_5'') which acts on the methylene-blue results from the two reactions $2H^{\cdot} + 2S_2O_3'' \rightleftharpoons 2HS_2O_3'$ and $2HS_2O_3' \rightleftharpoons S_4O_5'' + H_2O$, which are equivalent to $2H^{\cdot} + 2S_2O_3'' \rightleftharpoons S_4O_5'' + H_2O$. The rate of bleaching of methylene-blue, dx/dt, would then be given by the expression $dx/dt = k'$ [methylene-blue] $[S_4O_5''] = k$ [methylene-blue] $[S_2O_3'']^2[H^{\cdot}]^2$.

In other words, the rate of bleaching should be proportional to the square of the S_2O_3'' ion concentration, which, in dilute solutions, would be approximately equal to the thiosulphate concentration. If, then, in the solution under investigation, very little of the total thiosulphate was in the form of S_4O_5'', we should expect to find the rate of bleaching proportional to the square of the total thiosulphate concentration and also to the square of the hydrogen-ion concentration; but if practically all the thiosulphate were present as $H_2S_4O_5$ (or S_4O_5''), this would no longer be true, and the rate of bleaching would be directly proportional to the first power of the thiosulphate concentration (since the $H_2S_4O_5$ concentration would be simply half of this), and practically independent of the hydrogen-ion concentration. Intermediate results between these two extremes would correspond to the case where some thiosulphate was present as such and some as $H_2S_4O_5$.

From the results of Expt. U (Table VII), it is seen that, in the solutions of lowest acidity and lowest thiosulphate concentration, the times taken to bleach the constant amount of methylene-blue become closely proportional to the square of the (total) thiosulphate concentration. With the higher concentrations both of acid and of thiosulphate, the times of bleaching are intermediate between those required by a first-power and by a second-power effect of the thiosulphate. In all solutions less than 2·3*N* with respect to hydrogen chloride, the rate of bleaching is approximately proportional to the total acid concentration, and therefore, in all probability, to the hydrogen-ion concentration. 4·75*N*-Acid has no more effect than 2·3*N*, *i.e.*, above 2·3*N* the reaction seems to become independent of hydrogen-ion concentration. 9·5*N*-Acid is found actually to delay the bleaching as compared with acid of half its strength. This effect has probably nothing to do with hydrogen ions, but may well depend upon such factors as increased viscosity. Rough measurements of the viscosities of 10*N*- and 5*N*-hydrochloric acid show that these are in the ratio of 1·46, whereas the corresponding ratio for 5*N*- and *N*-acid is 1·15, showing that a marked increase of viscosity occurs above 5*N*. That the acid acts according to approximately the first power of its concentration might be regarded as indicating an ordinary catalytic effect, but we prefer to consider that this is due to the fact that, in so far as thiosulphate is present as such, the bleaching reaction depends on the square of the acidity, but in so far as it is present as S_4O_5'', the bleaching is independent of the acidity, where we have no means of measuring S_4O_5'' and S_2O_3'' separately and have to express ourselves in terms of total thiosulphate.

It must be pointed out that even in the least acidic mixtures the concentration of acid was about 50 times that of the thiosulphate. We consider that the close agreement between these experimental results and the deductions made above furnishes evidence in favour of the real existence of the compound $H_2S_4O_5$, and it would seem that under the conditions of the experiments at least half the total thiosulphate was present as $H_2S_4O_5$.

In view of the fact that hydrogen sulphide reduces methylene-blue, one could explain the kinetic results obtained in the weaker and less acid solutions on the basis of such reduction, the hydrogen sulphide being derived from reaction (IX); for it will be found that the rate of reduction in this case would be given by the expression

$$dx/dt = k'[\text{methylene-blue}][H_2S] = k[\text{methylene-blue}][S_2O_3'']^2[H^{\cdot}]^2$$

which is of the same form as that obtained above.

To explain the kinetic results obtained in the stronger and more acid solutions on this basis, it would be necessary to assume that a large proportion of hydrogen sulphide was present, which is certainly not correct. Moreover, both theory and experiment (see p. 1425 and Expt. N) indicate that reaction (IX) tends to predominate at low acidities, not high ones. It may be concluded, therefore, that the reduction of methylene-blue by acidified thiosulphate is not due to hydrogen sulphide.

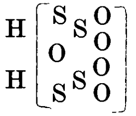
Since trithionic acid on hydrolysis can generate thiosulphate, as do also tetra- and penta-thionic acids, it is not surprising to find that in strongly acid solution trithionic acid slowly bleaches methylene-blue. It is possible that in this case some of the reduction is due to sulphoxylic acid (see p. 1447). The bleaching of the dye took several hundred times longer than in the parallel case with thiosulphate.

It should be noted that the observation that thiosulphuric acid can bleach indigo and methylene-blue greatly diminishes the value of such bleaching as a test for hydrosulphurous or sulphoxylic acid.

It is also important to realise that *sulphurous acid* is not without action on methylene-blue (and indigo). The strongest solutions (2—3*N*) act upon the methylene-blue or indigo in a similar way to concentrated hydrochloric acid, and very quickly, removing the blue colour and leaving only a pale purple or brown colour. This action, which appears to be due to the formation of addition compounds of acid and dye, falls off rapidly with dilution of the acid, whether this be hydrochloric or sulphurous acid. Even with 10*N*-hydrochloric acid it is only obvious when very little methylene-blue and an enormous excess of acid are used. In the case of sulphurous acid, it seems to be followed by a definite reducing action on the dye; this action is very slow, however, and is under investigation. We have satisfied ourselves that this action of strong hydrochloric acid or of sulphurous acid does not appreciably affect the results which we record in Expts. T and V.

The formation of tetrathionate from thiosulphate by methylene-blue in strongly acid solution furnishes a strong argument against the view that thiosulphuric acid can yield sulphoxylic acid according to the equation $H_2S_2O_3 + H_2O \rightleftharpoons 2S(OH)_2$ (see pp. 1405—6). Since sulphoxylic acid would probably be a very weak acid (like hypochlorous acid), strongly acidic conditions would be just those likely to favour such a change, were it possible. Experiments with sodium formaldehydesulphoxylate showed that, at the ordinary temperature, it bleaches methylene-blue relatively slowly in strongly acid solution, with formation of sulphite only (Expt. V). Were the bleaching action of the strongly acid thiosulphate solutions due to sulphoxylic acid, four times as much methylene-blue should be reduced as is actually observed.

It seems most probable that the acid $H_2S_4O_5$ is formed by the elimination of a molecule of water from two hydroxyl groups, not from one hydroxyl and one thiol group (which would probably give off a molecule of hydrogen sulphide to yield one form of trithionic acid). In this case it is to be regarded as having the structure



If, and when, either of the hydrogen ions ceases to be ionised, it can become attached by covalencies to either a sulphur or an oxygen atom. Three tautomeric structures are thus possible for the non-ionised $H_2S_4O_5$ just as two are possible for non-ionised thiosulphuric acid. Systematically $H_2S_4O_5$ might be called dithiopyrosulphuric acid.

Action of Sulphurous Acid and Hydrogen Sulphide on Thiosulphate.

Sulphurous acid and hydrogen sulphide are two acids which act upon thiosulphates in rather special ways, owing to their peculiar relationships to thiosulphuric acid and the polythionic acids.

The action of sulphurous acid is to cause the decomposition of thiosulphuric acid to take place much more in accordance with equation (IX). This it does partly by preventing reaction (VIII), of which it is a product, partly by forming the relatively stable, yellow addition compound, $H_2S_2O_3,SO_2$, and partly by removing hydrogen sulphide by reacting with it in accordance with equations (II*b*) and (I*b*). The sulphur resulting from reactions (II*b*) and (I*b*) does not, under favourable conditions, separate as such, but regenerates thiosulphate according to reaction (VIII). It is thus possible to get practically quantitative conversion of thiosulphate into trithionate, *e.g.*, by acting upon a saturated solution of potassium thiosulphate with strong sulphurous acid solutions at 30° (Hertlein, *Z. physikal. Chem.*, 1896, **19**, 292). Under ideal conditions the reactions which occur could be summarised by an equation such as $K_2S_2O_3 + 4SO_2 + H_2O = K_2S_3O_6 + H_2S_3O_6$. Action does not, of course, cease with the formation of trithionate. Continued action of sulphurous acid causes hydrolysis of trithionate, and ultimately sulphate and sulphur appear; tetra- and penta-thionate may be formed in the intermediate stages.

An elaborate investigation of the action of sulphurous acid on thiosulphate has been made recently by Foerster and Vogel (*loc. cit.*).

When hydrogen sulphide is passed into a solution of sodium thiosulphate, precipitation of sulphur occurs, slowly at the ordinary temperature, but more quickly on warming. This is due to decomposition of thiosulphuric acid displaced by the hydrogen sulphide and to the usual interaction of hydrogen sulphide and sulphurous acid (Reactions VIII*a*, II*b*, and I*b*). On heating, the solution becomes yellow, owing to the formation of polysulphide, and if the passage of hydrogen sulphide is discontinued, the whole of the precipitated sulphur ultimately dissolves. If the solution is boiled for a sufficient time, the yellow colour disappears, and the solution is then, as a rule, alkaline to phenolphthalein. If hydrogen sulphide is again passed in, more sulphur will be precipitated, and will dissolve on heating, and all the above operations can be repeated indefinitely.

During the boiling, all the reactions of decomposition which occurred during the passage of hydrogen sulphide are reversed with regeneration of thiosulphate, but during this period there is a tendency for sodium sulphide and sulphite to produce some free alkali owing to hydrolysis.

The Wackenroder Reaction and the Genesis of the Polythionic Acids.

If equation (II) is accepted as representing the way in which sulphoxylic acid changes into hydrogen sulphide and sulphurous acid, it follows with reasonable certainty that the first step in the interaction of hydrogen sulphide and sulphur dioxide in the Wackenroder reaction is the converse of this change. The first step would thus give sulphoxylic acid and its pyro-derivative, which would then be hydrolysed to sulphoxylic acid. Interaction of the latter with hydrogen sulphide would give rise to sulphur (reaction I*b*). The freshly formed sulphur would be in a very suitable form to react with sulphurous acid to produce thiosulphuric acid (reaction VIII), which, as has been mentioned already, is relatively stable from the point of view of this reaction in dilute, feebly acid solutions. Trithionate will then be formed from thiosulphuric acid according to reaction (IX) (see p. 1417), whilst it is not impossible that some trithionate may be formed in two steps from sulphurous acid and sulphoxylic acid by a reversal of the reactions considered on p. 1447, as has, in fact, been suggested by Foerster and Vogel (*loc. cit.*), who give a reaction $SO + 2HSO_3' \longrightarrow S_3O_6'' + H_2O$. We found that traces of polythionates were formed by shaking sulphurous acid with a solution of sulphur in benzene, whilst, by passing sulphur dioxide and sulphur vapour simultaneously into water, a solution $0{\cdot}32N$ with respect to sulphurous acid and about $0{\cdot}01N$ with respect to a mixture of tri- and tetra-thionic acids was obtained.

In the latest paper on the subject (*Z. anorg. Chem.*, 1926, **157**, 80), Foerster and Centner definitely conclude that, in some cases at least, trithionate cannot result from degradation of pentathionate, but must be formed directly. They favour a reaction $S_2O_3'' + 4HSO_3' + 2H^{\cdot} \longrightarrow 2S_3O_6'' + 3H_2O$, which corresponds to that given by us on p. 1440, and which can only be a summation equation.

If reaction (II) really is the first step in the Wackenroder reaction, all the peculiarities of the initial stages of the reaction which were noticed by Debus (J., 1888, **53**, 336) and Riesenfeld and Feld (*Z. anorg. Chem.*, 1921, **119**, 225) can be accounted for just as readily as on the basis of the primary reaction $H_2SO_3 + H_2S \rightleftarrows H_2SO_2 + H_2SO$, proposed by Heinze (*J. pr. Chem.*, 1919, **99**, 109), or of the reaction $H_2S + 2H_2SO_3 \rightleftarrows 3\{SO + H_2O\}$ suggested by Riesenfeld and Feld (*loc. cit.*), or that—$H_2S + H_2SO_3 \rightleftarrows H_2S_2O_2 + H_2O$—put forward by Foerster and Hornig (*loc. cit.*, p. 92). This matter has been considered by Foerster and Hornig (*loc. cit.*, pp. 87—90), and their explanation will suit our reaction as well as either of the above.

Riesenfeld and Feld's reaction is very similar to our reaction (II), since their $\{SO + H_2O\}$ is really sulphoxylic acid, but a termolecular reaction is much less probable than a bimolecular one.

No proof that sulphoxylic acid is a primary product of the Wackenroder reaction is available, but it is extremely probable that the bleaching of indigo by sulphurous acid solutions freshly treated with hydrogen sulphide is, in the main, due to sulphoxylic acid. This bleaching effect was first noted by Spring (*Bull. Acad. roy. Belg.*, 1878, **45**, 605; *op. cit.*, Vol. II, p. 1060), and we have confirmed it, but in view of the fact that thiosulphuric acid also bleaches indigo, methylene-blue, etc., such bleaching can only be regarded as a very uncertain test for either hydrosulphurous or sulphoxylic acid (see p. 1435).

Whilst the primary reaction in the Wackenroder solution is being considered, it may be pointed out that, since dry hydrogen sulphide and sulphur dioxide do not react, it is unlikely that the one is oxidised directly by the other. Even in presence of water vapour the mixed gases seem to be stable and only to react on the surface of the containing vessel—presumably in the film of adsorbed moisture. We have also found that when hydrogen sulphide is passed into liquid sulphur dioxide no interaction occurs; this is contrary to the statement of Quam (*J. Amer. Chem. Soc.*, 1925, **47**, 103), but agrees with Matthews's observations (*loc. cit.*). The mechanism we have suggested for the interaction of these two gases in presence of water cannot, of course, be applied to their interaction in presence of other dry liquids (Matthews, *loc. cit.*). Some complex other than pyrosulphurous acid must be involved in such cases, as suggested by Klein (*J. Physical Chem.*, 1911, **15**, 1).

Pentathionic acid has generally been regarded as the first thionic acid to appear, both in the case of the decomposition of thiosulphates by acids and in the Wackenroder reaction, tetra- and tri-thionic acids being subsequently formed from it by loss of sulphur. Debus (*loc. cit.*, pp. 339, 344) considered that in both these reactions the anhydride of pentathionic was formed by direct polymerisation of the anhydride of thiosulphuric acid : $5S_2O_2 = 2S_5O_5$, the necessary S_2O_2 being given by the addition of nascent sulphur to sulphur dioxide. In the Wackenroder reaction, some tetrathionic acid was formed directly according to the scheme $3SO_2 + H_2S = H_2S_4O_6$. In both reactions, he believed that tetra- and tri-thionic acids resulted from degradation of pentathionic acid.

All recent workers on polythionates seem to follow Debus, although there are several variants of the condensation which is supposed to produce pentathionic acid. Raschig ("Schwefel- und Stickstoff-Studien," 1924, pp. 273—304) assumes the polymerisation of S_2O_2 to $S_{10}O_{10}$, which gives pentathionic acid *via* the hypothetical $H_4S_{10}O_{12}$. Riesenfeld and Feld (*loc. cit.*, p. 252) assume that SO is first formed and gives S_5O_5 by polymerisation and thence pentathionic acid by hydration. Foerster and Hornig (*loc. cit.*) suggest an eleventh-order ionic variant of the above polymerisation, $5S_2O_3'' + 6H^{\cdot} \longrightarrow 2S_5O_6'' + 3H_2O$, and this appears to be accepted by the most recent workers in this field, Kurtenacker and Kaufmann (*loc. cit.*, p. 256).

Arithmetically, such polymerisations as the above are simple enough, and this seems to be the chief argument which has led to the suggestion that pentathionic is the first-formed thionic acid. Kinetically, the matter is very different, however, and the polymerisation could only occur in a series of steps. This difficulty has been realised by Foerster and Vogel (*loc. cit.*, p. 163), who now suggest that pentathionic acid is formed by a reaction $SO + 2HS_2O_3' \longrightarrow S_5O_6'' + H_2O$.

We have found that the first thionic acid to appear during the decomposition of thiosulphate by acids is trithionic, although it is generally accompanied by some tetrathionic. It is true that pentathionic acid may appear after a very short time, especially under drastic conditions (see p. 1433). All the observations made in this section of our work make it almost certain that pentathionic acid is the last to be formed, not the first, whilst the experiments and arguments brought forward up to this point are most in favour of the view that trithionic acid is the first to be formed (Expt. W).

When hydrogen sulphide and sulphurous acid interact in dilute solution, we also find that trithionic acid is the first thionic acid to appear, and we think there can be no doubt that, in the Wackenroder reaction also, tetra- and penta-thionic acids are built up from trithionic acid (Expt. X).

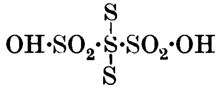
The Structural Formulæ of the Polythionates and their Hydrolysis in Acid and in Alkaline Solution.

Dithionic acid is not considered in this paper, as it is not formed under the conditions which give rise to the other thionic acids. The structure and mode of hydrolysis of trithionic acid have already been dealt with on pp. 1421, 1422.

Tetrathionic Acid.—The formation of tetrathionates from thiosulphates by oxidation leads naturally to the structure

$$OH\cdot SO_2\cdot S\cdot S\cdot SO_2\cdot OH$$

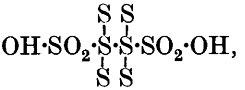
for tetrathionic acid, whilst the ease with which one atom of sulphur is removed from tetrathionate by sulphite to yield trithionate and thiosulphate (Colefax, J., 1908, **93**, 798) supports the structure $OH\cdot SO_2\cdot S(\cdot S)\cdot SO_2\cdot OH$. A study of the solid model suggests that the two formulæ are probably equally correct in the sense that the slight electronic adjustment needed for one form to pass into the other appears to offer no insuperable difficulty.

Pentathionic Acid.—For this acid the structure  $OH\cdot SO_2\cdot \overset{\overset{S}{|}}{\underset{\underset{S}{|}}{S}}\cdot SO_2\cdot OH$ seems definitely preferable to the alternative $OH\cdot SO_2\cdot S\cdot S\cdot S\cdot SO_2\cdot OH$. The chief arguments in its favour are (i) its compactness and symmetry, (ii) 3 of the 5 sulphur atoms have a co-ordination number of four, (iii) 2 atoms of sulphur are readily removed by sulphite to yield trithionate. The thionic acid formulæ with all the sulphur atoms in one straight chain were originally suggested by Mendeléev (*J. Russ. Phys. Chem. Soc.*, 1870, **2**, 276; 1871, **3**, 871), and they have been more or less accepted ever since, although it has been recognised that the evidence in support was slender.

Formulæ for sodium tri-, tetra-, and penta-thionates have been proposed by Raschig (*op. cit.*, p. 305), but there seems to be nothing in their favour and much against them. Martin and Metz (*Z. anorg. Chem.*, 1923, **127**, 91) also have proposed formulæ for the polythionates.

Many of the objections to the chain formulæ have been summarised by Vogel (J., 1925, **127**, 2248), who suggested the structures $OH\cdot SO_2\cdot S(\cdot S)\cdot SO_2\cdot OH$ and $(OH\cdot SO_2)_2{:}S\cdot S\cdot S$ for tetra- and pentathionic acids, respectively. With this formula for tetrathionic acid, tautomeric with the chain formula, we agree, but we consider that our formula for pentathionic acid is preferable to Vogel's, for the reasons given above.

In our opinion, it is the tendency of the central sulphur atom in trithionic acid to become co-ordinated with four other atoms in all, which is the prime cause of the readiness with which tetra- and penta-thionic acids are built up from trithionic. This building-up process comes more or less to an end with the symmetrical pentathionate, and on these grounds the existence of hexathionic acid is improbable. It is true that Debus (*loc. cit.*, pp. 301—309) thought he had some evidence for hexathionates, but no later worker has prepared either hexathionic acid or hexathionates. Higher polythionates than pentathionate only seem likely if the two central sulphur atoms in the straight-chain form of tetrathionic acid can add on additional sulphur atoms in the same way as does the one central sulphur atom of trithionic acid. The building-up process in this case would come to an end with octathionic acid,



$$OH{\cdot}SO_2{\cdot}\overset{S}{\underset{S}{S}}{\cdot}\overset{S}{\underset{S}{S}}{\cdot}SO_2{\cdot}OH,$$

with hexa- and hepta-thionic acids as intermediate stages. We have some experiments in progress which seem to suggest that this is actually possible.

The reactions of the polythionates are essentially reactions of hydrolysis and decomposition, and the formulæ proposed above offer a satisfactory explanation of all the facts observed. The hydrolysis of tri-, tetra-, and penta-thionic acids has been the subject of careful investigations by Foerster and Hornig (*loc. cit.*, p. 86) and by Kurtenacker and Kaufmann (*loc. cit.*, pp. 43, 369). Some of the difficulties which arise in connexion with the hydrolysis of trithionic acid have been dealt with on pp. 1421, 1422.

The nature of this hydrolysis is of importance in relation to that of tetra- and penta-thionic acids, for trithionic acid is invariably formed when they are hydrolysed. This seems to occur either by direct decomposition according to the reactions (XII*b*) and (XIII*b*), and perhaps $H_2S_5O_6 \rightleftharpoons H_2S_3O_6 + S_2$, or else by the intervention of sulphurous and thiosulphuric acids, which are products of the hydrolysis of trithionic acid, in accordance with the reactions (XIV), (XV), and (VIII).

In view of what has been stated on p. 1428 in connexion with reaction (VIII), it is very probable that the decomposition of penta- and tetra-thionic acids in accordance with reactions (XII) and (XIII) really follows a bimolecular course, and that the equations should therefore be doubled so as to indicate the formation of S_2 units.

The final products of acid hydrolysis of tri-, tetra-, or pentathionic acid are sulphuric acid, sulphur dioxide, and sulphur, a small quantity of hydrogen sulphide being formed in the intermediate stages. Kessler (*loc. cit.*) alludes to this formation of hydrogen sulphide, and we have noticed that it is always produced.

Under strongly alkaline conditions, the final result of hydrolysis can be represented by the equations

$$2H_2S_3O_6 + 3H_2O \rightleftarrows H_2S_2O_3 + 4H_2SO_3 \quad . \quad . \quad . \quad (a)$$
$$2H_2S_4O_6 + 3H_2O \rightleftarrows 3H_2S_2O_3 + 2H_2SO_3 \quad . \quad . \quad . \quad (b)$$
$$2H_2S_5O_6 + 3H_2O \rightleftarrows 5H_2S_2O_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

(Kurtenacker and Kaufmann, *loc. cit.*, p. 369), but in the case of tetra- and penta-thionates, the tri- and tetra-thionates are formed to some extent as intermediate steps, and in absence of sufficient hydroxyl-ion concentration some hydrolysis of trithionate in the manner characteristic of acid conditions occurs, with consequent formation of sulphate (see p. 1422).

In considering the above results, we wish to stress two important governing factors : (i) Tri-, tetra-, and penta-thionic acids are all of the nature of pyro- or anhydro-acids, and so would be expected to break up in alkaline solution or on dilution, and to be relatively more stable the more acid the solution. Complications are introduced by the instability of the products of hydrolysis, thiosulphuric and sulphurous acids, but the general correctness of these deductions is illustrated by the great difficulty in preparing pentathionates, owing to the readiness with which they decompose, although in strongly acid solution, pentathionic acid is the most stable of the three acids. (ii) The tendency for a sulphur atom to become co-ordinated with four other atoms is the second governing factor.

Equations (*a*), (*b*), and (*c*) above are only to be regarded as summation equations, but if we consider them for a moment as representing directly reversible reactions, and bearing in mind that thiosulphuric and tri-, tetra-, and penta-thionic acids are all strong acids, whilst sulphurous acid is much weaker, we see that the formation of pentathionic acid according to equation (*c*) would correspond to a much greater decrease of acidity than would the formation of either tri- or tetra-thionic acid according to equation (*a*) or (*b*). This is probably a main reason for the greater stability of pentathionic acid in acid solution, and its great instability under alkaline conditions.

In discussing the relative stability of compounds, it is most important to realise that this cannot be done in general terms, but only with reference to specified conditions—a matter which is frequently overlooked. Vogel's general statement (*loc. cit.*) that the relative stabilities of the polythionic acids should decrease in the order di-, tri-, tetra-, and penta- has no meaning, nor has Foerster and Centner's statement (*loc. cit.*, p. 56) that pentathionate is much less stable than tetrathionate.

The hydrolysis of the unsymmetrical form of trithionic acid has been dealt with on p. 1421, but the mechanism of the hydrolysis of the symmetrical form, which finally yields sulphite and thiosulphate, has not been considered. Since no sulphate is formed, it seems clear that in the first step the hydroxyl group becomes attached to the central sulphur atom, and not to a terminal one, yielding a molecule of sulphonic acid and an unstable intermediate compound which is to be regarded as thiopermonosulphuric acid :

$$\begin{array}{r:l} \mathrm{OH{\cdot}SO_2} & \mathrm{S{\cdot}SO_2{\cdot}OH} \\ \mathrm{H} & \mathrm{OH} \end{array} \longrightarrow \mathrm{H{\cdot}SO_3H + OH{\cdot}S{\cdot}SO_2{\cdot}OH}$$

Further hydrolysis of the thiopermonosulphuric acid yields sulphoxylic acid and another molecule of sulphonic acid: $\mathrm{OH{\cdot}S{\cdot}SO_2{\cdot}OH} + \mathrm{H_2O} \longrightarrow \mathrm{S(OH)_2} + \mathrm{H{\cdot}SO_3H}$. The sulphoxylic acid is then oxidised to sulphurous acid by another molecule of thiopermonosulphuric acid which is itself reduced to thiosulphate : $\mathrm{S(OH)_2} + \mathrm{OH{\cdot}S{\cdot}SO_2{\cdot}OH} \longrightarrow \mathrm{H_2SO_3} + \mathrm{H_2S_2O_3}$. The final result of the hydrolysis in alkaline solution is represented by equation (*a*) on p. 1446.

If this picture of the mechanism of the hydrolysis is correct, it should be possible to produce trithionate from sulphoxylic and sulphurous (sulphonic) acids. We attempted such a synthesis by boiling a solution of sodium formaldehydesulphoxylate (1 mol.) and sodium pyrosulphite (1½ mols.), but were unable to obtain any definite or conclusive results.

The hydrolysis of tetra- and penta-thionic acids is explicable along similar lines. The fact that pentathionate on treatment with sodium carbonate loses one atom of sulphur to form tetrathionate (Raschig, *op. cit.*, pp. 273—304), not two to form trithionate, suggests that in alkaline solution tetrathionate has the straight-chain structure, although it would seem to pass readily into the other form, $\mathrm{OH{\cdot}SO_2{\cdot}S({\cdot}S){\cdot}SO_2{\cdot}OH}$, since sulphite converts it into trithionate. Hydrolysis of the straight-chain form would yield 1 mol. of thiosulphate and 1 mol. of thiopermonosulphuric acid, which would then give rise to thiosulphate and sulphite, as already indicated. Complete alkaline hydrolysis of tetrathionate would thus take place in accordance with equation (*b*) on p. 1446.

In the case of pentathionic acid, the sulphur atom dropped in the very first step of all (equation XIII) suffices to convert a molecule of sulphite into thiosulphate, so that in this case complete alkaline hydrolysis yields nothing but thiosulphate [equation (*c*), p. 1446].

Acid hydrolysis of pentathionic acid may be expected to follow a different course. If the hydroxyl group becomes attached to the central sulphur atom, as in the case of trithionic acid, the first step would yield an intermediate product which can be regarded as dithiodithionic acid. This would, no doubt, be very unstable and might be expected to break up into sulphur and thiopermono-

$$OH{\cdot}SO_2{\cdot}S(\colon S_2){\cdot}SO_2{\cdot}OH \xrightarrow{H_2O} \underset{\text{sulphonic acid}}{H{\cdot}SO_2{\cdot}OH} + \underset{\text{dithiodithionic acid}}{OH{\cdot}S(\colon S_2){\cdot}SO_2{\cdot}OH}$$

sulphuric acid, which would then react further as indicated on p. 1447. It is possible that an intermediate compound $OH{\cdot}S({\cdot}S){\cdot}SO_2{\cdot}OH$ might similarly be formed by acid hydrolysis of the unsymmetrical form of tetrathionic acid, $OH{\cdot}SO_2{\cdot}S({\cdot}S){\cdot}SO_2{\cdot}OH$.

The influence of hydrogen-ion concentration on the relative stability of tri-, tetra-, and penta-thionic acids is not easy to forecast in any detailed manner. Reactions (XII) and (XIII) will only be dependent upon hydrogen-ion concentration in so far as the relative strengths of the three acids differ. Precise information on the strengths of these acids is lacking, although we know that they are all strong acids.

The strength might be expected to diminish in the order penta-, tetra-, tri-, in view of the fact that the content of "negative" sulphur diminishes in this order. If this is correct, decrease of acidity should tend to favour reactions (XII*a*) and (XIII*a*). The accepted statements (Debus, Raschig, *locc. cit.*) that alkali causes the formation of tetrathionate and sulphur from pentathionate, however, contradict this. It follows therefore that, either pentathionic acid is the weakest of the three acids, which is possible, or else that its decomposition into tetrathionic acid and sulphur is only apparent—that is to say, reaction (XIII*b*) does not occur directly at all, but only as the final result of a more or less complex series of changes [*e.g.*, slight hydrolysis in conjunction with reactions (XV*b*) and (VIII*a*)], some part of which is definitely favoured by decrease of acidity. In any case it is certain that the proportions of tri-, tetra-, and penta-thionic acids which can exist in a solution depend, among other things, upon the hydrogen-ion concentration, increase and decrease of which favour the formation of penta- and tri-thionic acid, respectively. The effect of change of acidity is so great that the separation of sulphur on addition of alkali is almost as delicate a test for pentathionate as is the ammoniacal silver nitrate test.

EXPERIMENTAL.

Expt. A. (Theory, p. 1403.)—Solutions containing known amounts of sodium formaldehydesulphoxylate, sodium hydroxide, and lead acetate were heated to boiling for a short time and allowed to cool. The mixture of lead sulphide and metallic lead was filtered off and washed, finally with alcohol, dried as quickly as possible at 100°, and weighed. It was then converted into lead sulphate and weighed again. The following results were obtained in three experiments :

	I.	II.	III.
Sodium formaldehydesulphoxylate (g.)	2·4	2·4	1·2
N/2-Lead acetate (c.c.)	5	5	5
2*N*-Sodium hydroxide (c.c.)	10	2	10
Molecular ratio, Pb/PbS, in precipitate	1·82	2·27	2·69

Sufficient water was added in the second and third experiments to make the total volume the same as that of the mixture used in the first experiment. The sodium formaldehydesulphoxylate used in this and following experiments had the composition NaCl, 10; $Na_2SO_4,10H_2O$, 6·1; $Na_2CO_3,10H_2O$, 21·1; CH_3O_3SNa, 62·8%. Chloride, sulphate, sulphoxylate, and total sodium were estimated, and carbonate (proved qualitatively) was calculated. The sulphoxylate was determined by the methods of Helwig (*Amer. Dyestuff Reporter*, 1920, **7**, ii, 12) and Hollingsworth Smith (*J. Amer. Chem. Soc.*, 1921, **43**, 1307), which gave the same results.

Expt. B. (Theory, p. 1405.)—A bright silver coin (92·5% Ag) was digested for 1 hour with sulphur, 1 c.c. of 0·3*N*-potassium dichromate, 1 c.c. of 2*N*-phosphoric acid, and about 20 c.c. of water. Very little sulphide attached itself to the coin; most remained mixed with the sulphur.

$$\left.\begin{array}{ll}\text{Loss of weight of coin} & = 0{\cdot}0079 \text{ g.}\\ Ag_2S \text{ produced} & = 0{\cdot}0078 \text{ g.}\\ \text{Sulphate formed, as } BaSO_4 & = 0{\cdot}0063 \text{ g.}\end{array}\right\} \begin{array}{c}\text{Molecular ratio,}\\ Ag_2S : BaSO_4 = 1{\cdot}17.\end{array}$$

Expt. C. (Theory, p. 1405.)—10 C.c. of a solution containing 0·2 g. of the sodium formaldehydesulphoxylate (= 0·1256 g. pure sulphoxylate) were mixed with 10 c.c. of 2*N*-sodium hydroxide, 5 c.c. of 0·5*N*-lead acetate, and 5 c.c. of 2*N*-barium chloride. After simmering for ½ hour in an atmosphere of purified coal gas, the mixture of lead sulphide, metallic lead, and barium sulphate was filtered off. The lead and lead sulphide were extracted with warm dilute hydrochloric acid, and the barium sulphate was weighed; 0·0146 g. was obtained, of which 0·0088 g. was due to sulphate present in the sulphoxylate used. Decomposition of sulphoxylate in accordance with a reaction $2H_2SO_2 \longrightarrow H_2S + H_2SO_4$ would yield 0·1242 g. of barium sulphate; 0·0058 g. is only 4·6% of this, and no importance can be attached to it.

Expt. D. (Theory, pp. 1403, 1405.)—(I) 20 C.c. of 1·25*N*-hydrochloric acid containing 0·315 g. of pure sulphoxylate were digested for 80 mins. in a small flask connected to two wash-bottles containing

N/10-iodine and a third containing *N*/40-thiosulphate. A slow current of purified coal gas passed through the apparatus. The iodine reduced was 82% of that required by a reaction $2H_2SO_2 \longrightarrow S + H_2SO_3 + H_2O$, which is a combination of reactions (I) and (II). After the precipitated sulphur had been filtered off, any sulphate formed during the decomposition was precipitated and weighed as barium sulphate; only 0·0163 g. was obtained, and as 0·022 g. was to be expected from the sulphate present in the sulphoxylate used, it is clear that no sulphate had been formed during the hydrolysis. The filtrate from the barium sulphate gave a reaction for pentathionate, and the formation of this and other thionic acids would account for only 82% of the calculated amount of sulphurous acid being obtained. The weight of sulphur precipitated in this experiment was difficult to estimate exactly owing to the presence of some trithioformaldehyde, but it also corresponded to about 82% of that demanded by the above equation. Another experiment, similar to the above, in which some lead acetate was added to the reacting solution gave practically identical results. No metallic lead or lead sulphide was precipitated and 0·0185 g. of barium sulphate was obtained.

(II) 10 C.c. of sulphoxylate solution (= 1 g. crude or 0·628 g. pure sulphoxylate), 20 c.c. of 1% arsenious oxide solution, and 10 c.c. of concentrated hydrochloric acid were boiled in a current of purified coal gas until the arsenious sulphide had coagulated, and then for a further 15 mins. to drive out sulphur dioxide. The sulphide was filtered off and weighed. The filtrate after considerable dilution and treatment with barium nitrate gave a very small precipitate of barium sulphate on standing [Found : As_2S_3, 0·1444 g. Calc. (from the weight of sulphoxylate used on the basis of reaction II) : 0·1447 g. Found : $BaSO_4$, 0·0226 g. Calc. (for sulphate present in the sulphoxylate used) : 0·044 g.].

Expt. E. (Theory, p. 1405.)—To a mixture of 20 c.c. of 1% arsenious oxide solution and 10 c.c. of concentrated hydrochloric acid were added 2 c.c. of 2*N*-thiosulphate. After the mixture had been boiled to expel sulphur dioxide, the precipitate, which consisted mainly of arsenious sulphide, was filtered off and weighed. Sulphate in the diluted filtrate was precipitated as barium sulphate (Found : As_2S_3, 0·0654 g.; $BaSO_4$, 0·3908 g.).

Expt. F. (Theory, p. 1408.)—100 C.c. of a solution containing 1·2289 g. of sodium hydrosulphite (of 88·7% purity) and 0·3750 g. of sodium carbonate were left exposed to the air at room temperature, and the unoxidised hydrosulphite was determined at intervals by Hollingsworth Smith's method (*loc. cit.*) : k is the value of the expression $1/t \, . \log_e a/(a - x)$.

t (mins.).	% $Na_2S_2O_4$ present.	$k \times 10^4$.
0	88·7	—
10	82·4	73·4
20	80·6	47·8
40	69·6	60·9
80	54·9	60·0
140	39·4	58·1
260	16·5	64·8

The rate of oxidation and the actual value of k will depend on the exact conditions of exposure, which were, however, approximately constant during the experiment.

Expt. G. (Theory, p. 1414.)—Analyses are given in Table I of a number of old sulphurous acid solutions, none of which had deposited any visible sulphur. Sulphurous and sulphuric acids were determined by iodine titration followed by estimation of total sulphate. Polythionic acids were estimated in a separate portion, from which sulphur dioxide had been expelled either by boiling or by means of an air current.

The method we have used for analysing mixtures of polythionic acids depends on one of the tests given by Takamatzu and Smith (J., 1880, **37**, 608), *viz.*, the addition of silver nitrate to the neutral or acid solution. The general reaction may be expressed $Ag_2S_xO_6 \longrightarrow Ag_2S + (x - 3)S + 2SO_3$, whence the molecular ratios of silver sulphide to free atomic sulphur precipitated are, for trithionate 1 : 0, for tetrathionate 1 : 1, and for pentathionate 1 : 2. Since colloidal and precipitated sulphur react slowly with silver nitrate to form silver sulphide, a standard solution of silver nitrate should be used in only very slight excess. Decomposition of the silver polythionates is rapid at temperatures near 100°, so it is best to heat the solution nearly to this temperature before adding the silver nitrate. The silver sulphide–sulphur precipitate, which filters easily, is well washed, finally with ammonia or ammonium carbonate solution. (This is to remove sulphuric acid, which otherwise is obstinately retained and causes charring of the filter paper on drying.) The precipitate is dried at 100° and weighed. A portion is then weighed into a glass ignition tube and heated until all free sulphur (if present) is driven off. Brilliant, black, crystalline silver sulphide remains and is weighed. This method, although simple and expeditious, gives surprisingly reproducible results, whilst it enables the presence of very small amounts of free sulphur to be detected with certainty owing to the dark colour of the distillate. Although the ratio $Ag_2S : S$ may be found to be 1 : 1, this does not prove the presence of pure tetrathionate unless it has been shown that pentathionate is absent, which can be most readily done by the well-known ammoniacal silver nitrate test.

It is to be noted that after sulphur dioxide had been expelled by an air current at the ordinary temperature, both tri- and tetra-

TABLE I.

Age of solution.	6 months.	1 year.	1¾ years.	2·5 years.	5 years.	12 years.
Original normality.	High, but not recorded.	Not recorded.	1·141	0·2688	High, but not recorded.	0·0996
Final normality :						
H_2SO_3	0·975	0·0855	0·567	0·055	0·0515	0·0680
H_2SO_4	0·201	0·0122	0·0542	0·0821	0·412	0·0236
$H_2S_3O_6$ } After boiling off SO_2.	—	0·0038	0·0005	0·0002	0·0101	0·0021
$H_2S_4O_6$ } After boiling off SO_2.	—	—	0·0013	—	—	—
$H_2S_2O_3$ } After displacing SO_2 with air current.	—	—	0·0056	—	—	—
$H_2S_3O_6$ } After displacing SO_2 with air current.	0·0002	—	—	—	0·0037	0·0011
$H_2S_4O_6$ } After displacing SO_2 with air current.	—	—	—	—	0·0029	0·0005
Remarks (based on known conditions of storage).	Mostly atmospheric oxidation.	Little, if any, atmospheric oxidation.		Much SO_2 had escaped through rubber tube and probably some atmospheric oxidation had occurred.	Much atmospheric oxidation known to have occurred.	Little, if any atmospheric oxidation.

TABLE IV.

The Hydrolysis of Potassium Trithionate in Neutral and in Acid Solution at Room Temperature.

(Calculated for 100 millimols. of $K_2S_3O_6$.)

										Conditions of expt.		
		S_3O_6''.	S_4O_6''.	S_5O_6''.	S_2O_3''.	HSO_3'.	SO_4'' developed.	S deposit.	Total S content (Theory, 300).	Acidity = $H^{\cdot}$ developed owing to hydrolysis.	Normality of $K_2S_3O_6$.	Time (days).	Solvent.
i.	(K. & K.)	44·5	25·0	0	6·5	27·2	31·5	0	305·2	41·3	0·184	28	Water
ii.	(B. & D.)	35·0	23·7	0	0	34·0	51·1	14·1	299·1	35·4	0·1	42	0·1N-H_2SO_4
iii.	(K. & K.)	9·8	30·0	0	0	73·0	54·0	26·7	305·2	27·0	0·184	28	N-HCl
iv.	(B. & D.)	0	19·3	1·6	0	56·4	105·6	57·0	303·3	98·0	0·05	280	0·05N-H_2SO_4

thionic acids were present, but after the sulphur dioxide had been boiled off only trithionic acid was found. We satisfied ourselves that these sulphurous acid solutions contained neither colloidal sulphur, thiosulphate, nor pentathionate. Only the 1¾-year old solution seemed definitely to contain thiosulphate. After the sulphur dioxide had been boiled off, both tri- and tetra-thionic acids were found in this case.

Expt. H. (Theory, p. 1416.)—Table II epitomises a series of experiments in which solutions of the concentrations stated were boiled for 2 minutes in a small conical flask, 20 c.c. being used in each experiment. Hydrochloric acid was used. The mouth of the flask was covered with a filter paper moistened in the centre with one drop of 2*N*-lead acetate solution. The stains of lead sulphide produced were compared and preserved.

In the more concentrated thiosulphate solutions, sulphur dioxide was evolved as well as hydrogen sulphide, which accounts for the fact that the latter appears to reach a maximum with *N*/100-acids, as shown in cols. 2, 3, and 4 of the table. Although the two gases can coexist in gaseous mixtures for considerable periods of time, lead acetate is not darkened when sulphur dioxide is largely in excess. The non-appearance of hydrogen sulphide under the conditions represented above the sloping line suggests that its production is due to a molecular rather than to an ionic reaction.

TABLE II.

Acid normality.	*N*-$Na_2S_2O_3$.	0·1*N*-$Na_2S_2O_3$.	0·01*N*-$Na_2S_2O_3$.	0·001*N*-$Na_2S_2O_3$.	0-0001*N*-$Na_2S_2O_3$.
1×10^{-7} (= H_2O)	H_2Sf, 0				
5×10^{-7}	H_2Sf, 0				
5×10^{-6}	H_2Sf, 0				
5×10^{-5}	H_2Sf, 0	H_2Sf, Ⓢ			
5×10^{-4}	H_2S, Ⓢ	H_2S, Ⓢ	H_2Sf, 0		
1×10^{-3}	H_2S, Ⓢ	H_2S, Ⓢ	H_2S, S		
5×10^{-3}	H_2S, Ⓢ	H_2S, S	H_2S, S		
1×10^{-2}	$\boxed{H_2S}$, S	$\boxed{H_2S}$, S	$\boxed{H_2S}$, S		
5×10^{-2}	H_2S, S	H_2Sf, S	H_2S, S	H_2Sf, 0	
5×10^{-1}	H_2Sf, S	S	H_2S, S	H_2S, 0	H_2Sf, 0
5	$\boxed{S}$	$\boxed{S}$	H_2S, S	$\boxed{H_2S}$, 0	$\boxed{H_2S}$, 0

Abbreviations :

0, no sulphur separated.

Ⓢ, sulphur appeared and later disappeared.

S, sulphur was permanently precipitated.

$\boxed{S}$ or $\boxed{H_2S}$, the substance appeared to have reached a maximum in respect to the *vertical column.*

H_2Sf, a *faint* stain due to hydrogen sulphide.

Expt. I.—(i) (Theory, p. 1418). 5·86 G. of hydrated sodium thiosulphate, 1 c.c. of 0·2N-sodium hydroxide, and 5 c.c. of water were boiled for 5 mins. and cooled; addition of sodium plumbite then gave an immediate brown coloration.

(ii) (Theory, p. 1418). 20 C.c. of an aqueous solution containing 1·4 g. of hydrated sodium thiosulphate and 20 c.c. of 2N-sodium hydroxide were heated to boiling for 50 mins. in an atmosphere of purified coal gas, then acidified with hydrochloric acid and boiled in coal gas to decompose thiosulphate and drive off sulphur dioxide. Sulphate present in the solution was then estimated as barium sulphate : 0·0030 g. was obtained (mean of three experiments) after subtracting (α) the barium sulphate (0·0020 g.) due to sulphate formed during the decomposition of the thiosulphate with acid, and (β) sulphate, silicate, etc. (0·0083 g.), derived from the action of alkali on the glass. Both corrections were determined separately.

A similar solution after boiling for 50 mins. in coal gas was treated with 5 c.c. of 0·5N-lead acetate solution. This gave an immediate brown colour, and after short heating lead sulphide coagulated and was weighed as sulphate. In another experiment the lead acetate was added before the boiling with alkali. The two results were identical (Found : $PbSO_4$, 0·0443 g.). This lead sulphate represents sulphide formed by reaction (IX), but corresponds to only 5·8% of the original thiosulphate. The sulphate also formed is derived from the hydrolysis of a small proportion of the trithionate formed in the main reaction.

(iii) (Theory, p. 1419). 1·4 G. of hydrated sodium thiosulphate, dissolved in 20 c.c. of 8·4N-caustic soda and boiled for 50 mins. in coal gas, gave the merest trace of sulphide on treatment with lead acetate. On large dilution with water no further precipitate appeared.

(iv) (Theory, p. 1419). 10 C.c. of 2N-caustic soda, 2·5 c.c of 2N-sodium sulphite, and 20 c.c. of 0·0072N-hydrogen sulphide were digested in coal gas for 1 hour at the b. p.; 1 c.c. of 0·5N-lead acetate solution was then added. An immediate black precipitate was formed which was filtered off and weighed as lead sulphate. A blank experiment using 2·5 c.c. of water instead of the sodium sulphite was also carried out (Found, from sulphite mixture: $PbSO_4$, 0·0273 g.; from blank : $PbSO_4$, 0·0260 g.).

(v) (Theory, p. 1419). 20 C.c. of 2N-caustic soda, 5 c.c. of 2N-sodium sulphite, and 1 c.c. each of 2N-sodium thiosulphate and 2N-sodium sulphide were boiled for 50 mins. in coal gas, and then treated with 5 c.c. of 0·5N-lead acetate. The lead sulphide precipitated was converted into 0·2886 g. of sulphate, whereas a blank experiment without sulphite and thiosulphate gave 0·2903 g.

(vi) (Theory, p. 1418). This experiment was similar to the last, but 2 c.c. of $2N$-sodium sulphate were used instead of the sulphite, and double the quantity of thiosulphate (*i.e.*, 2 c.c.) was used; 0·2885 g. of lead sulphate was obtained, again showing that no disappearance of sulphide had occurred during the boiling. Some thiosulphate was added, as it was thought that, if sulphide would not act directly on the sulphate, it might possibly react with thiosulphate to form trithionate, which would then react with the sulphide to form thiosulphate.

We could get no indication of any thiosulphate formation when hydrogen sulphide was allowed to act upon sodium sulphate either at the ordinary temperature or at 100°. Numerous experiments were made under various conditions of concentration, etc.

(vii) (Theory, p. 1418). 0·2988 G. of lead thiosulphate was boiled with 20 c.c. of $2N$-sodium hydroxide, in which it dissolved, in an atmosphere of hydrogen. There was no trace of darkening or precipitate after 50 mins'. boiling. 0·8250 G. of lead thiosulphate, when boiled in hydrogen with 25·9 c.c. of $0{\cdot}2N$-sodium hydroxide (*i.e.*, the equivalent amount of alkali), became cream-coloured, but showed no sign of sulphide formation after 10 mins'. boiling.

When lead thiosulphate is boiled with less than the equivalent amount of alkali, decomposition is rapid and large amounts of trithionate are obtained, but a considerable proportion of the trithionate is decomposed into sulphide and sulphate, with consequent neutralisation of the alkali used—in fact, the reaction mixture becomes slightly acid. The black precipitate obtained was shown to be a mixture of lead sulphide and sulphate with sometimes a little unaltered thiosulphate, a trace of which may also remain in the solution. The filtrate from the lead sulphide and sulphate precipitate was analysed for thiosulphate and trithionate, one portion being titrated with $N/100$-iodine, and the trithionate and thiosulphate in another portion being obtained from the weight of silver sulphide given on treatment with silver nitrate. The results of two such experiments are given in Table III.

TABLE III.

	I.	II.
PbS_2O_3 (g.)	0·9012	0·7126
H_2O (c.c.)	10	10
NaOH	1 c.c. $2N$.	5 c.c. $0{\cdot}2N$.
Ag_2S from trithionate (g.)	0·1680	0·1507
Ag_2S from thiosulphate (g.)	0·0135	0·0163

In both experiments, the mixture was boiled for 5 mins. in an atmosphere of hydrogen. In the second experiment, the mixture was left over-night after the boiling before filtering.

(viii) (Theory, p. 1418). Even under weakly acid conditions, some trithionate can survive during the decomposition of lead thiosulphate : 1·3974 g. of lead thiosulphate, 5 c.c. of 2·175*N*-acetic acid, and 20 c.c. of water were boiled for 5 mins.; sulphur dioxide was given off, and the black residue contained considerable free sulphur. The filtrate contained trithionate capable of giving with silver nitrate 0·0897 g. of silver sulphide, and thiosulphate equivalent to 0·0368 g. of silver sulphide (the thiosulphate was obtained by titration with *N*/100-iodine—some sulphurous acid may have been present, in which case the value for trithionate would be correspondingly greater).

Expt. J. (Theory, p. 1420.)—Freshly precipitated and washed manganese sulphide, obtained from the hydrated sulphate, was gently boiled in a narrow-mouthed, conical flask, closed by a funnel, with a solution of 10 g. of ammonium sulphate in about 50 c.c. of water, until all the sulphide had reacted, *i.e.*, for 3—5 hours. In Expts. I, III, and IV, 1·1 g. of $MnSO_4,4H_2O$ was used; in Expt. II, 2·2 g. Hydrogen was passed through the flask in which Expt. IV was carried out, but even so, indications of yellow ammonium sulphide were seen at the end of the exit tube inside the flask—a sign of slight oxidation. The sulphide used in Expt. I had undergone more oxidation during its preparation than the other samples. The filtrates from the small amounts of higher oxide of manganese (very small in Expt. III) were analysed by titrating one portion with *N*/100-iodine, and weighing the silver sulphide obtained with silver nitrate from another portion. The silver sulphide was shown to contain no free sulphur, and in amount it agreed very closely with that required by the iodine titration, showing that it was derived from thiosulphate, not trithionate :

	I.	II.	III.	IV.
Ag_2S weighed (g.)	0·1290	0·0662	0·0144	0·0048
Ag_2S calc. from iodine titration	(Not titrated.)	0·0669	0·0139	0·0050

A series of experiments in which hydrogen sulphide was passed through boiling strong solutions of ammonium magnesium and ammonium nickel sulphates gave entirely negative results, no trithionate or thiosulphate being formed.

Expt. K. (Theory, p.1421.)—The following is a typical experiment : Hydrogen sulphide was passed through a mixture of 5 c.c. of concentrated sulphuric acid and 3 c.c. of water for 70 mins. No sulphur was precipitated. The gas was then displaced from the solution by a very rapid current of hydrogen, and the solution was diluted rapidly to 100 c.c.; this caused an immediate opalescence due to sulphur. Some of the diluted solution, when tested with ammoniacal silver nitrate, gave a faint coloration such as would be expected from the sulphur cloud; the paleness indicated that all the hydrogen sulphide had been removed. The silver sulphide from half of the solution amounted to 0·0029 g. and the $N/100$-iodine titration indicated that one-third was derived from trithionate and two-thirds from thiosulphate. The cloud of sulphur formed on dilution is attributed to formation and decomposition of thiosulphate owing to the large addition of water having caused hydrolysis of trithionic acid originally present. In other experiments, it was noted that traces of hydrogen sulphide continued to be removed by the current of hydrogen from the original strong acid after several hours. This suggests a slow reversal of reaction (X) by the water present. The thiosulphate found in the solutions after dilution had probably been formed by hydrolysis from trithionate, partly during the removal of hydrogen sulphide by the current of hydrogen, and partly during the dilution.

Expt. L. (Theory, p. 1423.)—0·4884 G. of potassium trithionate and 20 c.c. of $5N$-hydrochloric acid were gradually heated to boiling. Sulphur appeared at about 50°. Boiling was continued until no more sulphur dioxide was liberated—about 25 mins. in all. The liberated sulphur weighed 0·0335 g. and a further 0·0032 g. separated on dilution owing to decomposition of pentathionic acid. This small quantity was filtered off after being boiled for 1 hour to cause coagulation. Sulphate present in the filtrate gave 0·4817 g. of barium sulphate, whereas if 1 mol. of trithionate gave 1 mol. of sulphate, the weight would have been 0·4216 g.

Expt. M. (Theory, p. 1423.)—Potassium trithionate solutions of the concentrations given in Table IV (p. 1452) were left at room temperature for the stated periods and then analysed. Our polythionate estimations (B. and D.) were made by the silver nitrate method (see Expt. G), whereas Kurtenacker and Kaufmann (K. and K.) used volumetric methods.

It is evident that N-hydrochloric acid had hastened the hydrolysis to a later stage in 28 days than had $N/10$-sulphuric acid in 42 days. Obviously our experiment (iv) represents the latest stage of the four —again confirming our contention that pentathionic acid is the last polythionic acid to be produced. Kurtenacker and Kaufmann also expected this, but had not reached it in (iii).

Expt. N. (Theory, p. 1425.)—Four mixtures of sodium thiosulphate and hydrochloric acid of the composition stated in Table V, (i), (ii), (iii), and (iv) were made by adding 1 c.c. of M-sodium thiosulphate to 10 c.c. or 21 c.c. of hydrochloric acid of appropriate strength in small, tightly-corked flasks. After the stated intervals of time, the whole mixture was titrated with $N/10$-iodine, a separate

TABLE V.

Extension of Holleman's Experiments.

(*a*) 0·5M-$Na_2S_2O_3$ = a; 1·0N-HCl.

t.	N/10-Iodine, c.c.	$BaSO_4$ (g.).	x.	x (alternative calc.).	k.
0·5	11·95	0·0611	0·165	0·154	1·97
1	12·8	0·0816	0·210	0·221	1·45
2	13·9	0·1097	0·276	0·308	1·23
4	14·35	0·1316	0·348	0·343	1·15
5	14·6	0·1381	0·363	0·363	1·06
6	14·5	0·1416	0·383		
7	14·2	0·1432	0·410		
43 hrs.	10·25				

(*b*) 0·25M-$Na_2S_2O_3$ = a; 0·5N-HCl.

t.	N/10-Iodine, c.c.	$BaSO_4$ (g.).	x.	x (alternative calc.).	k.
1	12·1	0·0528	0·060	0·121	1·26
2	13·2	0·0895	0·113	0·147	1·65
5	13·9	0·1217	0·153	0·225	1·59
10	14·0	0·1462	0·215	0·231	2·46
15	14·1	0·1541	0·228	0·237	2·75
20	14·2	0·1615	0·243	0·243	6·94
30	13·8	0·1623			
240	12·6	0·1750			
43 hrs.	9·75				

(*c*) 0·1M-$Na_2S_2O_3$ = a; 0·2N-HCl.

t.	N/10-Iodine, c.c.	x.	k.
0·5	10·5	0·0091	2·00
1	10·7	0·0128	1·47
5	11·9	0·0347	1·06
10	12·8	0·0511	1·02
15	13·1	0·0566	0·87
17	13·2	0·0584	0·83
18	13·1	58·4% Decomposed at 17 mins. according to sulphate estimation after the iodine titration.	
20	12·7		
25	11·9		
30	11·7		
43 hrs.	9·25		

(i) 0·0455M-$Na_2S_2O_3$ = a; 0·196M-HCl.

t.	N/10-Iodine (c.c.).	x.	k.
1	10·5	0·00437	2·33
3	10·9	0·00785	1·53
5	11·2	0·0105	1·32
7	11·8	0·0158	1·66
10	11·95	0·0176	1·32
15	12·6	0·0228	1·47
20	13·13	0·0274	1·66
30	13·7	0·0324	(2·70)
40	14·2	0·0368	(2·31)
60	14·8	0·0420	(4·39)
80	15·1	0·0446	(13·62)
120	15·2	—	—
			Mean 1·61

Limiting val. used for calc., 15·2.

(ii) 0·0455M-$Na_2S_2O_3$ = a; 0·393M-HCl.

t.	N/10-Iodine (c.c.).	x.	k.
1	10·55	0·00463	2·49
3	11·0	0·00842	1·66
5	11·4	0·0118	1·54
7	11·85	0·0156	1·64
10	12·4	0·0202	1·76
15	12·85	0·0240	1·64
20	13·6	0·0303	2·19
30	14·5	0·0379	(3·65)
			Mean 1·85

Limiting val. used for calc., 15·4.

TABLE V. (*contd.*)

(iii) 0·091M-$Na_2S_2O_3 = a$;
0·393M-HCl.

t.	N/10-Iodine (c.c.).	x.	k.
1	10·9	0·0152	2·20
5	12·4	0·0404	1·76
10	13-4	0·0573	1·87
15	14·1	0·0691	2·31
20	14·3	0·0725	2·15
35	14·6	0·0775	1·81
40	14·85	0·0817	(2·42)
60	15·4		
80	15·2		
120	15·1		
		Mean	2-02

Limiting val. used for calc., 15-4.

(iv) 0-091M-$Na_2S_2O_3 = a$;
1·96M-HCl.

t.	N/10-Iodine (c.c.).	x.	k.
1	11·5	0·0182	2·75
3	13·1	0·0376	2·58
5	14·0	0·0485	2·51
7	14·6	0·0546	2·36
10	15·3	0·0643	2·65
15	15·7	0·0692	2·33
20	16·3	0·0764	2·88
30	17·0	0·0849	(5·10)
40	17·3	0·0886	(10·14)
60	17·4	0·0898	(13·74)
80	—		
120	17·2		
		Mean	2·58

Limiting val. used for calc., 17·5.

mixture being used for each titration. The amount of iodine required at zero time was, of course, 10 c.c. in each case. In these experiments, since excess of acid was used, it can be safely assumed that decomposition of thiosulphate was complete when the iodine titration had reached its limiting value. The amount of decomposition at earlier stages was calculated by simple proportion. Holleman's three experiments, in which equivalent amounts of thiosulphate and acid were used, were also repeated (Expts. *a*, *b*, and *c*). At the time stated, a known quantity of N/10-iodine was added and the excess was then titrated with N/10-thiosulphate. After 1 min. we obtained similar results to his, but we followed up the experiments in order to determine the maximum values of the titre so that the velocity coefficient might be calculated in the manner indicated on p. 1428. For this purpose, the sulphate present in the titrated solution was also determined. In experiments (*a*) and (*b*) the sulphate was determined at each stage (and is given in the table as g. of barium sulphate) in order to get a direct measure of the amount of decomposition to compare with that calculated by simple proportion from the iodine titre and the sulphate formed at the stage of maximum iodine titre.

In all these experiments, which were carried out at 17°, the initial concentrations shown are those which obtained after mixing. Time, t, is given in minutes, unless otherwise stated. The number of mols. of thiosulphate decomposed is given by x; and k is the bimolecular velocity coefficient calculated from $k = x/ta(a - x)$.

Expt. O. (Theory, p. 1430; Fig. 1.)—Mixtures were made of 1 c.c. of 0·05, 0·1, 0·25, 0·5, or 1·0M-sodium thiosulphate with 10 c.c. of hydrochloric acid (or, in the cases indicated, phosphoric acid) of the *molecular* normalities shown on the abscissæ of Fig. 1, where the results are given in the form of curves. As ordinates are plotted the times (in mins.) required for the first appearance of visible sulphur, which could not, of course, be determined with very great accuracy. The actual normalities of thiosulphate and of acid in the mixture would be 10/11ths of those indicated. The experiments were done at room temperature (about 17°).

Expt. P. (Theory, p. 1432.)—Four separate mixtures were made, each containing 1 c.c. of each of the specified constituents: (1) 0·1*M*-Thiosulphate, 0·5*N*-hydrochloric acid, water: Sulphur deposition began 90 secs. after mixing. (2) 0·1*M*-Thiosulphate, 0·5*M*-potassium tetrathionate, 0·5*N*-hydrochloric acid: This remained absolutely clear for 24 hours after mixing. It then gave a strong reaction for pentathionate. The original tetrathionate contained only a faint trace of pentathionate. (3) 0·5*M*-Thiosulphate, 0·5*M*-sulphuric acid, water: Sulphur deposition started in 15 secs. and was soon very heavy. (4) 0·5*M*-Thiosulphate, 0·5*M*-potassium tetrathionate, 0·5*M*-sulphuric acid: Faint sulphur deposit after 2 mins. It was only slight after 10 mins. Concentrations are stated in molecular normalities in all cases. Since we made these experiments, similar ones have been recorded by Foerster and Centner (*loc. cit.*, pp. 64, 68).

Expt. Q. (Theory, p. 1432.)—0·203 G. of iodine in 20 c.c. of alcohol was mixed with 0·216 g. of potassium trithionate in 20 c.c. of water, and hydrogen sulphide was then passed in very slowly until the iodine was decolorised. Some sulphur was deposited, which was filtered off, washed, dried, and found to weigh 0·0153 g. To the filtrate was added 0·265 g. of lead nitrate in 20 c.c. of water. After standing for 5 hours, the lead iodide was filtered off and washed once. The filtrate from this iodide was warmed with 5 c.c. of 0·4*N*-silver nitrate and the precipitated mixture of silver sulphide and iodide and free sulphur was dried, weighed, and gently heated in an ignition tube. In this way it was found to contain 0·0104 g. of free sulphur. It represents the tetrathionate formed by direct addition of sulphur. The iodine used in the experiment would have liberated 0·0256 g. of sulphur, so that 40·6% was absorbed. In a second experiment using twice as much trithionate, 60·2% of the sulphur was absorbed.

Expt. R. (Theory, p. 1434.)—One c.c. of 0·05*M*-sodium thiosulphate and 10 c.c. of 0·25*N*-hydrochloric acid gave a deposit of sulphur in 9½ mins. When this mixture was neutralised by caustic soda after 7 mins., no precipitation of sulphur occurred either then or after ½ hour. In a second experiment, 1 c.c. of lanthanum nitrate solution was added after 7 mins., but no precipitate occurred until after 13 mins. On the other hand, neutralisation of the above mixture after 9 mins. caused an immediate opalescence and so also did addition of 1 c.c. of lanthanum nitrate solution after 9 mins.

When 1 c.c. of 0·1*M*-thiosulphate and 10 c.c. of 0·25*N*-hydrochloric acid were used, sulphur separated 5 mins. after acidification. Similar mixtures were neutralised with sodium hydroxide 2 mins. and 3 mins. after acidification. No sulphur had separated after an hour, but a precipitate formed when the neutralisation was effected after 4 or 4½ mins.

One c.c. of 0·1*M*-thiosulphate and 10 c.c. of 2·163*N*-hydrochloric acid deposited sulphur in 4 mins. 10 secs. To a similar mixture, 3 c.c. of 8*N*-caustic soda were added 3 mins. after acidification. An immediate opalescence was produced. This faded and disappeared after 2 mins. The solution was finally alkaline. One c.c. of 0·1*M*-thiosulphate and 10 c.c. of 5*N*-hydrochloric acid gave a deposit of sulphur in 15 mins. A similar mixture was carefully neutralised with 8*N*-caustic soda in presence of phenolphthalein within a few minutes of preparation. No immediate precipitation of sulphur occurred, but a faint opalescence appeared 13½ mins. from the start, and disappeared after a further minute. A somewhat similar result was obtained with 0·5*M*-thiosulphate and 5*N*-hydrochloric acid.

Expt. S. (Theory, p. 1435.)—In the following experiments 1 c.c. of *M*-thiosulphate and 10 c.c. of 10·5*N*-hydrochloric acid were mixed. (In the first experiment, 10 c.c. of 9*N*-acid were used.) The mixtures were left at room temperature for the times specified (in Table VI) in tightly-corked, small flasks. They were then titrated with 0·1*N*-iodine. In the first four experiments this was done in the concentrated mixture, without using starch and in presence of the precipitated sodium chloride. In the case of Expts. 2, 3, and 4, owing to the large amount of sulphurous acid present, the yellow iodide–sulphur dioxide complex was formed. Addition of a little water towards the end of the titration broke this down and enabled the end-point to be determined sharply. The solutions were then raised to boiling point to coagulate sulphur, which was filtered off and weighed. The filtrate was diluted considerably and reheated, and sulphate present was precipitated and weighed as barium sulphate. This sulphate is due to oxidation of sulphurous acid by iodine, but may be partly due to hydrolysis of thionic acids during the heating, etc. In Expt. 5 the solution was diluted with 50 c.c. of water before being titrated with iodine.

TABLE VI.

Expt.	Time elapsed before titration.	*N*/10-Iodine (c.c.).	$BaSO_4$ (g.).	Sulphur deposited (g.).
1	10 mins.	12·5	0·0714	—
2	2 hours	12·1	0·1082	0·0206
3	21 ,,	11·1	0·1559	0·0290
4	23·5 ,,	10·7	0·1663	0·0326
5	23·5 ,,	10·2	0·1175	0·0242

In the mixture used in Expt. 1, sulphur began to appear after 11 min. 50 sec.; some was seen just before the end of the titration with iodine. In the other experiments, most of the sulphur separated during the titration (owing to the consequent dilution) and subsequent heating, indicating that it originated from pentathionate.

If we assume that the reduction of iodine is due to sulphurous acid and thiosulphuric acid (or $H_2S_4O_5$) only, we can make the following deductions. In Expt. 1, 63·7% of thiosulphuric acid had remained unchanged (as $H_2S_4O_5$, in our opinion), and 30·6% had decomposed according to reaction (VIII). This assumes that all the barium sulphate had resulted from sulphurous acid and that no hydrolysis of polythionate had occurred. In Expt. 2, again assuming no hydrolysis of polythionate, 28·3% of thiosulphuric acid (as $H_2S_4O_5$) had remained, whilst 46·4% had decomposed according to reaction (VIII).

In Expts. 3, 4, and 5 it appears that no thiosulphuric acid remained in the cold solution, and if that is correct, the determinations show that: (α) In (3), 55·5% had decomposed according to reaction (VIII), and none remained undecomposed. Of the polythionate present in the cold mixture an amount corresponding to 0·0264 g. of barium sulphate had been decomposed during the boiling.

(β) In (4) and (5), 53·5% and 51%, respectively, had decomposed according to reaction (VIII). In (5), the barium sulphate obtained was equivalent to the iodine used, showing that no hydrolysis of polythionate had occurred during the boiling of the diluted solution; but in (4), where the boiling lasted longer than in (3), polythionate corresponding to 0·0414 g. of barium sulphate had been decomposed.

It should be noted that actually more thiosulphuric acid will have decomposed according to reaction (VIII) than is shown by the residual sulphurous acid, for some of the latter will have reacted with hydrogen sulphide, formed by reaction (IX), to yield sulphur (reactions II*b* and I*b*). The amount of thiosulphuric acid which has reacted to form polythionate cannot therefore be obtained by deducting from the original amount that remaining undecomposed and that which has decomposed in accordance with reaction (VIII).

Expt. T. (Theory, p. 1436.)—(i) An aqueous solution of methylene-blue was prepared containing 0·64 g. per litre (= 1/500th g.-mol. $C_{16}H_{18}N_3SCl$). One c.c. of 0·1*M*-sodium thiosulphate was added to 10 c.c. of hydrochloric acid, which was either 10*N*, 5*N*, or 2·5*N*. With each strength of acid two mixtures were made. To one, 24·5 c.c. of the methylene-blue solution were added, and to the other 25·5 c.c., the mixtures being in tightly-corked flasks filled with carbon dioxide. In each case, the solutions containing 24·5 c.c.

of methylene-blue were bleached, whilst those containing 25·5 c.c. retained a pale blue colour. The thiosulphate used in the experiment could reduce 25 c.c. of the methylene-blue solution according to the equation given on p. 1435.

Another bleaching experiment was done in a slightly different way, using a solution which was 0·1*M* with respect to thiosulphuric acid without any excess of other acid, obtained by mixing equal volumes of 0·2*M*-sodium thiosulphate and 0·4*M*-hydrochloric acid; on shaking this solution with solid methylene-blue in an atmosphere of carbon dioxide, it was found to bleach exactly the amount calculated from the equation, but no more.

0·32 G. of methylene-blue was dissolved in 100 c.c. of water and the solution placed in a separating funnel filled with carbon dioxide; 2 c.c. of *M*-sodium thiosulphate were added, followed by 10 c.c. of 2·5*N*-hydrochloric acid. The mixture was well shaken, and the colour disappeared completely in ½ hour; 9·84 c.c. of 2·564*N*-sodium hydroxide were then added, this being the amount required to produce neutrality after due allowance for the fact that 1 mol. of hydrochloric acid is liberated from methylene-blue for each mol. of the *leuco*-compound produced, whilst, on the other hand, each mol. of tetrathionate formed corresponds to the neutralisation of 2 mols. of hydrochloric acid. Immediately on addition of the alkali a white, flocculent precipitate was thrown out, which dissolved at once in ether. The ethereal extract was separated and the ether distilled in a current of carbon dioxide, leaving the *leuco*-methylene-blue as long, colourless crystals. These do not melt, but decompose on heating. They slowly turn blue owing to oxidation. The *leuco*-compound is strongly basic and cannot be extracted from acid solution by ether, although it is freely soluble in absence of acid. Bernthsen (*Ber.*, 1883, **16**, 1025; *Annalen*, 1885, **230**, 147) prepared it by reduction of methylene-blue with hydrosulphite ($Na_2S_2O_4$) followed by ether extraction.

Expt. U. (Theory, p. 1437.)—The times taken for the disappearance of the blue colour from mixtures of thiosulphate, hydrochloric acid, and methylene-blue were carefully noted, the thiosulphate being added last of all and the timing starting from then. These times are given (in secs.) under *t* in Table VII; they are the average of two or more concordant readings and are subject to an experimental error of at least 5%. The temperature was 15° throughout, and the same weight of methylene-blue (*viz.*, 0·0064 g.) was used in each experiment.

The total volume in each experiment was 21 c.c., 1 c.c. of *N*-, 0·5*N*-, or 0·2*N*-thiosulphate being added to 20 c.c. of 10*N*-, 5*N*-, 2·5*N*-, 1·25*N*-, 0·625*N*-, or 0·5*N*-hydrochloric acid containing the methylene-blue. The resulting normalities are shown in the table. (In this experiment, $N = \frac{1}{2}M$ for thiosulphate.)

TABLE VII.

Times of disappearance of colour from 0·0064 *g. of methylene-blue in solutions containing thiosulphate and hydrochloric acid of concentrations given in horizontal and vertical columns, respectively.*

	Conc. of HCl.	Column 1. 0·0476N-$H_2S_2O_3$. *t.*	Column 2. 0·0238N-$H_2S_2O_3$. *t.*	Column 3. 0·00952N-$H_2S_2O_3$. *t.*
a.	9·50N	41	104	450
b.	4·75N	20·3	61·4	250
c.	2·38N	21·6	61·8	265
d.	1·19N	37	117	840
e.	0·594N	78	230	1740
f.	0·475N	90	330	2160

The amounts of thiosulphate used in columns 1, 2, and 3 are, respectively, 8, 16, and 40%, since 0·0064 g. of methylene-blue has been shown to react with 40% of the weight of thiosulphate in column 3.

Aqueous solutions of methylene-blue can be kept without change of concentration or behaviour for more than a year. The solutions in 10N- and in 5N-hydrochloric acid, when freshly made, react with thiosulphate to give colourless solutions, but if they are kept for 3 days before mixing with thiosulphate, the reaction ceases before the solution is colourless, a green tint remaining. Dilute solutions of hydrochloric acid will dissolve only a portion of the methylene-blue, even although left for many days. All experiments with concentrations lower than 10N-hydrochloric acid were carried out by mixing an aqueous solution with appropriate amounts of acid just before the start, and usually it was found that no "salting out" of methylene-blue occurred in the short time the experiment lasted. When "salting out" does occur, it may begin soon after the addition of thiosulphate, and if so the experiment must be started afresh.

The following table gives the figures in Expts. *d*, *e*, and *f* (of Table VII) relatively to the 37-minute value for *d* 1, which is taken as unity, on the assumption that the variations are inversely as the square of the thiosulphate concentrations and also as the first power of the hydrochloric acid concentrations.

	(1.)	Theory.	Ratios.	(2).	Theory.	Ratios.	(3).	Theory.
d.	1	1	(1)	3·16	4	(1)	22·7	25
e.	2·108	2	(2·14)	6·75	8	(2·07)	47·0	50
f.	2·43	2·5	(2·82)	8·93	10	(2·56)	58·3	62·5

Expt. V. (Theory, p. 1439.)—One c.c. of 0·0628M-sodium formaldehydesulphoxylate was added to 10 c.c. of 10N-hydrochloric acid, and the times taken to bleach successive amounts of a methylene-blue solution containing 0·00064 g. per c.c. were noted. The sulphoxylate should have been able to bleach 31·4 c.c. of the methylene-blue if oxidation gave sulphite alone.

25 C.c. were bleached in 133 mins.; 27 c.c. (total) were bleached in 172 mins.; 29 c.c. (total) in 215 mins.; 31 c.c. (total) in 285 mins.; 33 c.c. (total) in 415 mins. The reaction was then complete.

Expt. W. (Theory, p. 1443.)—Polythionic acids were formed in thiosulphate solutions which had been acidified under varying conditions. The polythionates were not estimated individually, but on the basis of the S/Ag_2S ratio, as explained in Expt. G. Before the polythionates can be satisfactorily determined by this method, it is necessary to remove sulphurous acid or to render it inactive towards silver nitrate. In most cases this was done by boiling, which, unfortunately, has two undesirable effects: some polythionate is hydrolysed, and at the same time higher polythionates are formed at the expense of lower ones. These two effects are the more pronounced the greater the acidity of the solutions.

In a few experiments formaldehyde was added (compare Kurtenacker and Bittner, *Z. anorg. Chem.*, 1924, **141**, 297). This enables the polythionates to be determined directly by the silver nitrate method without any previous boiling. In another case, sulphur dioxide was removed by means of a brisk air current before the silver nitrate reaction was carried out.

When considered collectively, the experiments recorded in Table VIII show that trithionic acid is formed in the earlier stages of the decomposition, but that time, acidity, and boiling all tend to shift the balance in favour of pentathionic acid.

In Table VIII the columns numbered I—IX are given by the following key:

I. Normality of thiosulphate (*i.e.*, referred to $\frac{1}{2}Na_2S_2O_3$).
II. Nature and normality of acid used (referred to $1H_3PO_4$ or $\frac{1}{2}H_2SO_4$).
III. Precipitated sulphur (mg.).
IV. Silver sulphide (mg.).
V. Mg. of sulphur mixed with silver sulphide.
VI. Molecular ratio, S/Ag_2S.
VII. Molecular ratio of trithionate to tetrathionate (taken as 100).
VIII. ,, ,, ,, pentathionate ,, ,, ,, ,, .
IX. Ratio of sulphur, %, in polythionate to that in original thiosulphate.

Expt. X. (Theory, p. 1443.)—Solutions of sulphurous acid and hydrogen sulphide of known strength were prepared. Mixtures of

TABLE VIII.

		Experimental results.			*Calculations from experiments.*				
I	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	Observations.
0·5	0·518*N*-Phosphoric acid.	121·9	147·2	9·1	0·479	108	—	20·6	Boiled for 20 mins. immediately after mixing.
„		110·5	179·1	18·9	0·819	32	—	27·5	Left for 23 hours; then boiled for 20 mins.
„		126·7	183·5	11·5	0·485	106	—	25·8	Mixed slowly, acid added in 11 stages in 30 mins., then boiled for 20 mins.
„		123·4	195·5	10·7	0·424	136	—	27·0	Mixed slowly, thiosulphate added in 11 stages, then boiled for 20 mins.
„		104·3	214·1	25·1	0·909	10	—	35·0	Acid and thiosulphate left to mix by diffusion for 45 hours, then boiled for 20 mins.
„		93·7	333·3	32·1	0·747	34	—	50·3	Acid and thiosulphate left to mix by diffusion for 214 hours, then boiled for 20 mins.
	1·5*N*-Phosphoric acid.	134·8	46·6	8·4	1·363	—	57	8·25	Boiled for 20 mins. immediately after mixing.
„ *		133·1	53·9	8·3	1·193	—	24	9·1	Boiled for 20 mins. immediately after mixing.
„		131·6	52·9	10·0	1·465	—	85	9·5	Left for 23 hours; then boiled for 20 mins.
„		131·6	50·8	9·8	1·495	—	98	9·2	Mixed slowly, acid added in 11 stages in 30 mins., then boiled for 20 mins.
„		86·0	235·0	41·0	1·352	—	54	41·2	Acid and thiosulphate left to mix by diffusion for 45 hours, then boiled for 20 mins.
„		88·0	249·5	41·7	1·295	—	42	43·2	Acid and thiosulphate left to mix by diffusion for 216 hours, then boiled for 20 mins.
„	0·55*N* Sulphuric acid (Isohydric with 1·5*N*·H_3PO_4).	133·6	58·5	8·8	1·165	—	20	9·8	Boiled for 20 mins. immediately after mixing.
„		123·4	87·5	14·6	1·324	—	48	15·1	Left for 23 hours and then boiled for 20 mins.
„		110·8	166·2	28·3	1·319	—	47	29·9	Mixed and left for 45 hours, then boiled for 20 mins.
„		129·4	71·9	10·8	1·164	—	20	12·1	Mixed slowly, acid added in 11 stages in 30 mins., then boiled for 20 mins.
„		114·6	192·3	29·4	1·178	—	22	32·4	Acid and thiosulphate left to mix by diffusion for 45 hours, then boiled for 20 mins.
„		105·3	249·4	36·1	1·122	—	44	41·0	Acid and thiosulphate left to mix by diffusion for 216 hours, then boiled for 20 mins.
„		6·2	124·8	4·0	0·243	311	—	16·3	Excess of formalin added immediately after mixing; no boiling.†
„		97·4	321·8	17·6	0·424	135	—	44·4	Excess of formalin added after 5 hours' standing; no boiling.
„		126·5	128·6	17·4	1·049	—	5	21·0	Excess of formalin added after 23 hours' standing; no boiling.
„		116·0	179·0	12·7	0·553	81	—	25·6	SO_2 removed by brisk current of air bubbled through for 1¼ hours directly after mixing; no boiling.
0·16	1·4*N* Acetic acid.	65·8	31·5	2·8	0·396	152	—	4·7	Left at room temperature for 37 hours, then kept simmering for 1 hour. 30% of thiosulphate remained. The calculation is for the 70% decomposed.
0·5	0·52*N*	56·2	6·9	0·6	0·678	47·5	—	1·0	Kept at about 75° for 24 hours, boiled for 20 mins. 64% of thiosulphate remained. The calculation is for the 36% decomposed.
0·33‡	2·9‡	155·7	212·3	15·0	0·735	36	—	29·3	Result of a 5-hour distillation, 10 c.c. *N*-$Na_2S_2O_3$ with 40 c.c. 4·25*N*-acetic acid. Considerable hydrolysis with formation of H_2SO_4 occurred. Total sulphur in all products estimated, good sulphur balance obtained. 15% of thiosulphate remained. The calculation is for the 85% decomposed.

* In this experiment the phosphoric acid was 1·2*N*.

† The formalin stopped the reaction. Only 20% of the thiosulphate had been decomposed (iodine titration). The figures refer to this 20%. The iodine titration of thiosulphate in presence of formalin takes a considerable time (Schmidt, *Ber.*, 1907, **40**, 865).

‡ These normalities represent approximate average—acetic acid distilled over and hydrogen sulphide was evolved continuously. The volume of the solution in the distillation flask was kept approximately constant by the slow addition of 4·25*N*-acetic acid.

TABLE IX.

The Interaction of Solutions of H_2SO_3 *and* H_2S *in Various Concentrations and Proportions, and for Various Times.*

Normalities when mixed,		Molar ratio, SO_2/H_2S.	S ppt. in cold.	S ppt. on heating.	No. of c.c. used.	Duration of action.	From polythionic acid (g).		$S/Ag_2S = r$.	% of polythionate produced (referred to H_2S employed).	Remarks.
H_2SO_3.	H_2S.						Ag_2S	S			
0·0323	0·00375	8·4	Slight cloud, none ppd.		100	10 hrs.	Small amount.	0	0		The figures in the last column are calculated on the basis of a reaction $H_2S + 8SO_2 + 2H_2O = 3H_2S_3O_6$ and the assumption that $3Ag_2S$ would be obtained by the $AgNO_3$ reaction for each H_2S converted to polythionate.
0·0728	0·0028	26	Faint cloud after 15 mins. Clear in 23 hours.	None.	100	23 ,,	0·0172	0	0	16·6	
0·227	0·0088	26	Cloud persists for 40 hours.	None.	30	40 ,,	0·0209	0·0019	0·704	21	The whole mixture, including the cloud of precipitated sulphur, was boiled. There was complete disappearance of S on boiling due to formation of $H_2S_4O_6$ *while boiling.* ($r = 0·704$ gives $H_2S_3O_6 : H_2S_4O_6 = 0·42 : 1.$)
0·227	0·0073	31	Cloud.	None.	50	10 days	0·0517	0	0	37·9	Only the clear solution boiled in this case.
0·235	0·0106	22	Heavier cloud.		100	1 day	0·0451	0·0029	0·5	13·72	Total volume, 280 c.c.; *final deposit of* S *after* 12 *days* = only 0·0342 g. In this set of experiments evidence was obtained to show that no H_2SO_4 is produced in the original action before heating (to drive off excess of SO_2); also by means of iodine added to the *cold* solution and subsequent treatment with $AgNO_3$ it was *proved* that *neither* $H_2S_2O_3$ *nor* $H_2S_4O_6$ was in the *cold* solution after 10 days, since the precipitate consisted only of AgI and Ag_2S without any free sulphur. The $H_2S_4O_6$ is produced during the process of boiling. The *amount* of polythionate from *tri-* upwards increases with *time.*
0·235	0·0106	22	Deposit.	Sulphur cloud appeared after boiling some time.	20	10 days	0·0149	0·0011	0·572	18·91	
0·235	0·0106	22	Total wt. = 0·0342 g. (in 280 c.c.).	A *small* deposit, not weighed.	100	12 ,,	0·0898	0·0040	0·459	22·7	
1·25	0·0205	61	Cloud (total wt. = 0·0240 g.).	A deposit = 0·0128 g. on *total.*	200	6 ,,	0·1966	0·0185	0·729	12·8	No pentathionic acid was present in original *cold* solution.
1·41	0·0113	124	0·0302 g.	0·0156 g.	300	12 ,,	0·1087	0·0101	0·725	8·6	The yield of polythionate is less than before, whilst *r* is higher.
0·0235	0·0205	1·1	0·0621 g.	0·0013 g.	200	14 ,,	0·0818	0·0058	0·545	5·4	This mixture in ratio for reaction $5H_2S + 5SO_2 = H_2S_5O_6 + 5S + 4H_2O$ *gave no trace of pentathionate.* The solution after 14 days was still clouded. The S deposited was much *higher,* and the conversion into polythionate *lower,* than in any previous experiment.

these in different proportions were made and kept in tightly-corked flasks for various times. Excess of sulphur dioxide and hydrogen sulphide was then removed by boiling, and the polythionic acids present were estimated by the silver nitrate reaction (Table IX).

Summary.

(1) The hydrolysis of sulphur probably occurs in accordance with the equation $S_2 + 2H_2O \rightleftharpoons H_2S + (HO)_2S$.

(2) Sulphoxylic acid is very unstable either in acid or in alkaline solution, and readily yields hydrogen sulphide and sulphurous acid. The mechanism of this change and its bearing on the initial step in the Wackenroder reaction are discussed.

(3) The cause of the yellow colour of certain simple sulphur compounds is attributed to the presence of a sulphur atom with a ten-electron sheath.

(4) The decomposition of hydrosulphurous acid, $H_2S_2O_4$, is discussed.

(5) The autoxidation of sulphurous acid is considered.

(6) The main part of the paper deals with the decomposition of thiosulphuric acid, and it is shown that this decomposition can occur in three different ways.

(7) One mode of decomposition yields hydrogen sulphide and trithionic acid. This is considered to be an essential step in the Wackenroder reaction also, and trithionic acid is regarded as the primary thionic acid both in the thiosulphate decomposition and in the Wackenroder reaction.

(8) The objections to the usual view that pentathionic acid is the primary thionic acid are dealt with.

(9) It is shown that, in all probability, thiosulphates never decompose directly into sulphide and sulphate, but that the sulphate results from trithionate formed first of all.

(10) Experiments are recorded which suggest that the decomposition of thiosulphuric acid into sulphurous acid and sulphur is probably a bimolecular reaction involving a sulphur unit S_2.

(11) A new mode of decomposition of thiosulphuric acid into an anhydro-acid, $H_2S_4O_5$, is described. The new acid reduces methylene-blue and is thereby oxidised to tetrathionic acid.

(12) The structural formulæ of the polythionic acids and their behaviour on hydrolysis have been considered, and some new points of view put forward.

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