A Study of the Oxidation of Aqueous Sulfide Solutions by Chlorine.

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A STUDY OF THE OXIDATION OF AQUEOUS SULFIDE SOLUTIONS

BY CHLORINE

A DISSERTATION

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LESTER COLE FAULKENBERRY

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ABSTRACT

The purpose of this investigation was to determine the effect of the variables concentration, temperature, and pH on the reaction of hypochlorite and sulfide solutions.

By quantitative considerations it has been shown that if the solution is not too acid or too basic, sulfur and sulfate are produced in amounts depending upon the above mentioned variables. In solutions of pH of two or lower, it has been found that no sulfur exists in the solution as a final product but that there is a quantitative conversion of sulfide to sulfate. In very basic solutions sulfate is again the only product.

From a study of the effect of concentration a mechanism has been evolved to explain the simultaneous appearance of sulfur and sulfate in the reaction mixtures. By the application of the laws of kinetics in a qualitative way, experiment and postulate have been shown to agree.

In general it is found that if the concentration of sulfide is greater than the concentration of hypochlorite, the formation of sulfur is favored; and, if the concentration of hypochlorite is the greater, the formation of sulfate is favored. If the concentrations of the reactants are essentially the same, the ratio of sulfur to sulfate remains approximately constant. All of these facts are in agreement with the postulated mechanism.

The effect of increased temperature is to increase the proportion of sulfate formed, this increase being
approximately a direct function of temperature up to about 50° C. Above this temperature there is a rapid increase in the amount of sulfate formed. The rapid increase at higher temperatures is probably due to the secondary action of base on colloidal sulfur.

A study of the effect of pH on the course of the reaction reveals the fact that at pH values of two or less there is a quantitative conversion of sulfide to sulfate. As the pH increases sulfur appears in the reaction mixtures reaching a maximum at about ten. Above this pH an increase in sulfate formation occurs, and in very basic solutions, there is a quantitative conversion of sulfide to sulfate.

This effect of pH requires the postulation of two different mechanisms, one in acid and one in basic solution, the increase in sulfate content in both cases being explained by a secondary reaction of so-called "active" sulfur. In basic solution this secondary reaction is with the hydroxyl ion, while in acid solution chlorine monoxide is assumed to be the active agent in converting a portion of the active sulfur to sulfate before it can polymerize to colloidal sulfur.

The mechanisms have been developed both from the experimental results and from a consideration of analogous reactions in the literature. The reactions in basic solution are represented as follows:

\[ \text{Na}_2\text{S} + \text{NaOC}l + \text{H}_2\text{O} = \text{S} + \text{NaCl} + 2\text{NaOH} \]
\[ S + S = S_2, \text{ etc. to colloidal sulfur} \]

\[ S + NaOCl = SO + NaCl \]

\[ SO + NaOCl = SO_2 + NaCl \]

\[ SO_2 + H_2O = H_2SO_3 \]

\[ H_2SO_3 + NaOCl = H_2SO_4 + NaCl \]

\[ 8S + 6NaOH = 2Na_2S_3 + Na_2S_2O_3 + 3H_2O \]

\[ Na_2S_2O_3 + 4NaOCl + 2NaOH = 2Na_2SO_4 + 4NaCl + H_2O \]

\[ Na_2S_2 + NaOCl + H_2O = 3S + NaCl + 2NaOH \]

\[ S + NaOH, \text{ etc.} \]

In acid solution the reactions are as follows:

\[ H_2S + HOCl = S + HCl + H_2O \]

\[ S + S = S_2, \text{ etc. to colloidal sulfur} \]

\[ 2HOCl = H_2O + Cl_2O \]

\[ S + Cl_2O = SO + Cl_2 \]

\[ Cl_2 + H_2O = HOCl + HCl \]

\[ SO + HOCl = SO_2 + HCl \]

\[ SO_2 + H_2O = H_2SO_3 \]

\[ H_2SO_3 + HOCl = H_2SO_4 + HCl \]

Where the data was available the reactions were studied from the standpoint of free energy changes and it was shown by calculations of the free energy changes involved in the reactions, that they were all spontaneous reactions.
INTRODUCTION

This work was originally undertaken to develop a commercially feasible method for the removal of sulfide as a contamination of natural waters, the ultimate aim being the complete removal of the sulfur by oxidation to sulfate, precipitation, and subsequent filtration. Transformation of the sulfide to sulfate without removal of the sulfate will only produce a temporary removal since there exist certain types of bacteria which reduce sulfates to sulfides.

The original purpose was to effect the oxidation of sulfide to sulfate with chlorine, precipitate the sulfate with a suitable precipitant and filter out the precipitate. However, a preliminary study of the oxidation of alkali sulfides with chlorine or sodium hypochlorite showed that the oxidation of sulfide to sulfate was not complete except under certain conditions.

The preliminary experimental work on this problem was carried out by T. W. Ray Johnson (1) and J. G. Stevens (2). Both found that in basic solution sulfur appears as one of the products of the reaction, but if the solution be sufficiently acid there is a quantitative conversion of sulfide to sulfate. Stevens determined this critical pH to be about two. Above this value he found tests for sulfur, sulfate, and sulfide when one equivalent of hypochlorite is
added to one equivalent of sulfide. He also determined the critical temperature at which the sulfur produced by the reaction goes back into solution instantaneously. This temperature he found to be about 68° C.

The above results appeared to give promise of a rather interesting study, this study to be more of a theoretical nature, however. It appeared that there was some type of reaction mechanism in effect which was dependent upon the pH of the medium in which the reaction was occurring. Also, there appeared to be a quite interesting temperature effect.

The data of Johnson and Stevens was insufficient in scope to arrive at any definite conclusions as to the mechanism of the reaction. The present work was, therefore, undertaken as an expansion of the above work in an attempt to arrive at a better understanding of the effect of the variables, concentration, temperature, and pH on the reaction, and if possible to propose a satisfactory mechanism which would explain the experimental facts.

The following investigation is divided into three general parts:

1. Study of the effect of concentration.
2. Study of the effect of temperature.
3. Study of the effect of pH.
REVIEW OF THE LITERATURE

Early in this work it became evident that, exclusive of the general review of the literature with respect to the oxidation of sulfides in solution, a more or less thorough knowledge of the oxy-acids of sulfur would be necessary. The author also desired some knowledge of the various compounds of sulfur and chlorine since hypochlorites in acid solution contain considerable free chlorine.

Consequently, the literature was reviewed according to the following classification, those compounds which did not appear likely to have any connection with this work being later omitted in the general discussion of the literature:

1. Oxidation of Sulfides in Solution
2. Colloidal Sulfur
3. Sulfurous acid
4. Sulfuric Acid
5. Thiosulfuric Acid
6. Sulfoxylic Acid
7. Hyposulfurous Acid
8. Dithionic Acid
9. Trithionic Acid
10. Tetrathionic Acid
11. Pentathionic Acid
12. Hexathionic Acid
13. Pyrosulfurous Acid

\[
\begin{align*}
S & \quad H_2S_\text{O}_3 \\
H_2S_\text{O}_4 & \\
H_2S_\text{O}_5 & \\
H_2S_\text{O}_6 & \\
H_2S_\text{O}_7 & \\
H_2S_\text{O}_8 & \\
H_2S_\text{O}_9 & \\
H_2S_{10}O_8 & \\
H_2S_{10}O_9 & \\
H_2S_{10}O_{10} & \\
H_2S_{10}O_{11} & \\
\end{align*}
\]
14. Disulfuric Acid \( S_2O_3(OH)_2 \)
15. Pyrosulfuric Acid \( H_2S_2O_7 \)
16. Sulfur Chlorides \( S_2Cl_2, SCl_2, SCl_4, S_2Cl_4 \)
17. Thionyl Chloride \( SOCl_2 \)
18. Sulfuryl Chloride \( SO_2Cl_2 \)
19. Disulfuryl Chloride \( S_2O_4Cl_2 \)
20. Chlorosulfonic Acid \( SO_2Cl.OH \)
21. Hypochlorous Acid \( HOCl \)

The extent of the review of the above topics depends upon their bearing upon the present investigation.

1. Oxidation of Sulfides in Solution

NOTE: The literature is rather prolific in articles relative to the oxidation of gaseous hydrogen sulfide for the purposes of recovery of sulfur and elimination of it as a nuisance, but comparatively little work has been done on the oxidation of hydrogen sulfide and soluble sulfides in solution, and most of this work is of a qualitative or semi-quantitative nature.

L. N. Vauquelin (3) found that an aqueous solution of hydrogen sulfide is slowly oxidized by exposure to air forming water and milk of sulfur as well as some sulfuric acid. E. Filhol (4) said that no sulfuric acid is formed but if sufficient alkali-lye be present to form sodium hydrosulfide, the oxidation occurs more slowly, forming sulfur, alkali polysulfide and sulfate. J. Raab observed that light favored the reaction.

According to L. J. Thenard (6) an aqueous solution of hydrogen sulfide is decomposed by hydrogen peroxide as follows:
$$H_2O_2 + H_2S = S + 2H_2O$$

A. Classen and O. Bauer (7) stated that, if the above reaction is carried out in the presence of base, sulfate is produced.

G. Lunge and G. Billitz (8) observed that an aqueous solution of hydrogen sulfide is oxidized by hypochlorous acid to water, sulfuric acid, hydrochloric acid, and chlorine.

W. Feit and C. Kubierschky (9) found that a solution of hydrogen sulfide is oxidized by iodic acid to water, sulfur, and iodine; bromic acid yields water, sulfur, and bromine; alkali iodates yield water, sulfur, sulfuric acid, and iodine; and alkali bromates give as products water, sulfur, sulfuric acid, and bromine.

H. Prins (10) found that hydrogen sulfide reacts in the cold with chlorosulfonic acid with the separation of sulfur and the evolution of hydrochloric acid. When the mix is distilled sulfur monochloride and sulfur trioxide collect in the receiver.

J. W. F. Johnson (11) and C. Leconte (12) observed that hydrogen sulfide reduces dilute nitric acid yielding sulfur, sulfuric acid, ammonium sulfate, and nitric oxide.

G. Lunge and G. Billitz (13) stated that hydrogen sulfide is oxidized to sulfuric acid by aqua regia.

M. Gorlich and M. Wichmann (14) said that the following reaction takes place when hydrogen sulfide reacts with a solution of potassium nitrite:

$$KNO_2 + 3H_2S = KOH + 3S + NH_3 + H_2O$$
Aqueous solutions of sodium sulfide are oxidized in air, and sodium thiosulfate is formed. E. Mitscherlich (15) said that half of the sodium sulfide is converted into thiosulfate.

F. W. Durkee (16) found that thiosulfate is first formed in the electrolysis of sodium sulfide solutions and finally sodium sulfate. A. Scheurer-Kestner (17) and M. Merle (18) did not confirm the intermediate formation of the thiosulfate. M. Trautz and K. T. Volkman (19) have also studied the reaction, and F. Thomas (20) the effect of different colored light.

When a solution of sodium sulfide is oxidized with potassium nitrate, G. Lunge (21) and P. Pauli (22) found that sodium thiosulfate is first formed and at a higher temperature, sulfate.

When oxidized with potassium permanganate, M. Honig and E. Zatzeck (23) found that sulfur, sulfate, and tri-thionate are formed in the cold; only sulfate is formed in the hot solution.

A. Stromeyer (24) found that sodium bicarbonate reacts with sodium sulfide yielding hydrogen sulfide.

A. Mailfert (25) found that ozone converts the alkali sulfides to sulfate.

H. A. Krebs (26) observed that the rate of oxidation of hydrogen sulfide or alkali sulfide solutions is greatly accelerated by the presence of minute amounts of heavy metal sulfide such as nickel sulfide.
J. L. Bullock and G. S. Forbes (27) have made an extensive study of the oxidation of sodium mono- and poly-sulfides by certain aromatic nitro compounds. They made particular use of sodium m-nitrobenzenesulfonate in one tenth molar solution and at room temperature. The results of this work show that thiosulfate is the end product; sulfite was never obtained. It is shown that thiosulfate is not a direct oxidation product of the reaction and that the first products are hydroxyl ion and sulfur. The sulfur formed is taken up by the sulfide to form polysulfides until the hydroxyl ion-polysulfide ion ratio reaches a certain value, when the formation of thiosulfate proceeds uniformly. The sulfides used in these experiments were prepared by heating sulfur in aqueous sodium hydroxide to complete solution, and always contained a large amount of thiosulfate. By running the reaction in a borax-boric acid buffer solution of pH of about eight, elemental sulfur could be obtained with only a slight simultaneous formation of thiosulfate.

The total reaction is represented as:

\[ \text{pH} \]

1. \[ S + \text{RNO}_2 + \text{H}_2\text{O} = \text{S}_2\text{O}_3^{2-} + \text{RNH}_2 \]

The following mechanism is proposed:

2. \[ 3\text{HO}^+ + \text{RNO}_2 + 3\text{H}_2\text{O} = \text{6OH}^- + \text{3S} + \text{RNH}_2 \]

3. \[ S_\text{v} + \text{S} = S_{\text{v}-1} \]

4. \[ 6\text{OH}^- + 12S = 3\text{S}_2\text{O}_3^{2-} + 2\text{S}^2^- + 3\text{H}_2\text{O} \]

According to equation 2 there should be a definite pH which would allow the oxidation to progress without favoring the
formation of thiosulfate. This was found to be close to pH of eight.

Reaction 4 takes place rather rapidly at elevated temperatures even with ordinary rhombic sulfur but at 25° the reaction is slow unless the sulfur is in an "active" state—set free by an oxidation of sulfide or in some similar way.

While reduced temperature slows down the rate of oxidation (Reaction 2), the effect is much more pronounced in thiosulfate formation (Reaction 4). Below 25° the solution of sulfur is so slow that the greater part of it is precipitated in an unreactive form even in excess of hydroxyl ion. If an oxidation of disulfide is carried out slowly no appreciable amount of thiosulfate is formed until the system is saturated with sulfur; on the other hand, in the normal case where equal concentrations of sulfide ion and nitro compound are added together at the start, about thirty percent of the initial sulfide is oxidized in the first minute. Under these conditions there is a large amount of sulfur present in the active state at any particular time during the first few minutes. This sulfur would normally be dissolved by the sulfide ion present, but the large concentration of hydroxyl ion also present slows down this process and forms thiosulfate and regenerates polysulfide from the "active" sulfur.

S. A. Shchukarev and E. M. Kireeva-Tuzulakhova say that oxidation of sodium hydrosulfide by oxygen at atmos-
pheric pressure produces sodium thiosulfate, sulfite, and sulfate. The reaction appears to occur at the liquid gas interface and is of zero order. The reaction rate is inversely proportional to the initial concentration. Thiosulfate and sulfite are produced by parallel reactions and the sulfite reacts further to give sulfate. Sodium thiosulfate oxidizes very slowly, forming sulfite, sulfur, and sulfate. A mixture of thiosulfate and sulfite oxidizes with an increase in rate for thiosulfate and a decrease in rate for the sulfite. Oxidation of hydrogen sulfide is much more rapid than that of hydrosulfide and only sulfuric acid is formed. Sodium sulfide is oxidized to thiosulfate, sulfite, sulfate, and probably trithionate. The order of the reaction is anomalous. Sulfite and sulfate are formed to a greater extent than from the oxidation of hydrosulfide; altogether, thiosulfate is always the chief product. A rise in temperature increase the rate of these reactions.

The milky liquid formed by passing hydrogen sulfide through an aqueous solution of sulfur dioxide has been investigated by H. W. F. Wackenroder (29). The reaction may be represented by the equation:

$$2\text{H}_2\text{S} + \text{SO}_2 = \text{S}_2 + 2\text{H}_2\text{O}$$

However, the reaction is more complicated than this since it has been shown that the so-called Wackenroder's solution contains, in addition to colloidal sulfur, all the thionic acids from dithionic to hexathionic—H. Debus (30)—as well as some sulfuric acid.
The amount of polythionic acids formed, as well as the temperature, is of great importance in determining the degree of dispersion of the sulfur particles. Under conditions where considerable pentathionic and hexathionic acids are formed in accordance with the above equations, most of the sulfur is colloidal according to H. Bassett and R. G. Durrant (31).

I. G. Farbenind (32) has patented a process for the oxidation of metal sulfides to the corresponding sulfate by treating an aqueous sludge of the sulfide with oxygen or gases containing oxygen at a raised temperature and pressure, a mixture of sulfides being used as the starting material. The tendency to oxide formation is thus reduced and the oxidation accelerated. Thus an aqueous sludge of zinc sulfide and nickel sulfide is oxidized to the corresponding sulfates in five to seven hours by treatment with oxygen at 200° and 15 atmospheres pressure.

R. Kuhn (33) has patented a process for the removal of hydrogen sulfide from gases. Gases such as illuminating, coke oven, or producer gas are washed with water or an alkaline solution such as sodium carbonate and the solution of hydrogen sulfide or sodium sulfide is treated with a solution of catalyst and then treated with oxygen effecting the oxidation to thiosulfate. Among suitable catalysts are those prepared by mixing an alcoholic solution of 1-oxyanthraquinone with ammonical copper hydroxide to form the complex copper salt.
A process for the electrolytic oxidation of metal sulfides has been patented by G. N. Libby (34). Oxidation of pyrite or other conducting sulfides is effected by employing them as anode in an alkaline solution such as sodium or calcium hydroxide while supplying oxygen either by electrolytic decomposition of the solution or by constituting a battery of the Bunsen cell type by opposing another half cell or more electropositive material, preferably material which can be regenerated by oxygen of the air. Such a depolarizer may be formed of concentrated nitric acid surrounding an electrode of iron. The action of the latter effects the formation of nitric oxide which oxidizes readily with oxygen and water to regenerate the nitric acid. When FeS₂ is employed as anode it is oxidized to ferric hydroxide and sodium sulfate with the production of nearly the theoretical amount of energy.

R. S. Dean (35) has studied the oxidation of sulfides with potassium iodate. By experiments on hydrogen sulfide water and on lead sulfide it is shown that a large excess of iodate completely oxidizes the sulfur to sulfate independent of the concentration of hydrochloric acid provided it be strong enough to prevent hydrolysis of ICl. For cadmium sulfide, lead sulfide, and zinc sulfide the equation was found to be:

\[ 3X_2 + 2KIO_3 + 12HCl = 3XCl_2 + 2S + H_2SO_4 + 2KCl + 3ICl + 5H_2O \]

When a smaller concentration of hydrochloric acid was present the amount of iodate corresponded more nearly
\[
2\text{KIO}_3 + 6\text{HCl} = 2\text{KCl}_2 + 2\text{S} + \text{KCl} + \text{ICl} + 3\text{H}_2\text{O}
\]

where \(\text{A}\) stands for the metals above. Experiments show the progress of the reaction in the presence of varying amounts of hydrochloric acid. If hydrochloric acid is from 3 to 6 normal and a large excess of iodate used, oxidation quantitatively to sulfate is realized.

M. Pollacci (36) found that a paste of sulfur and water is oxidized by the air at 25-30° to sulfuric acid. This action is accelerated by (a) movement of the air, (b) sunlight. A paste kept in an atmosphere of hydrogen was not oxidized; from this the author concludes that the oxidizing action is not due to a decomposition of the water. He attempts to show by experiment that the action is to be ascribed to ozone rather than to oxygen of the air or hydrogen peroxide. From a study of the oxidation of the sulfides the author concludes: (a) All sulfides are oxidized by the air even below 30°. (b) The action is accelerated by sunlight, movement of the air, and above all by fine pulverization. (c) Oxygen is not fixed to form sulfate; the sulfur is set free, with the formation of the corresponding oxide. (d) The sulfur thus set free is oxidized thus, as is shown by the deposition of sulfur from waters containing hydrogen sulfide on contact with air. To prove that sulfur is set free from metallic sulfides carefully prepared sulfides are allowed to stand in the air and washed with carbon disulfide; this then, on evap-
oration, leaves crystals of sulfur. The ease of oxidation varies greatly with different sulfides. The author points out a source of error in quantitative analysis of drying sulfides at 100° and finally proposes a method for obtaining sulfur from natural waters.

2. Colloidal Sulfur

As shown by H. Moissan (37), sulfur exposed to air at ordinary temperatures, is slowly oxidized with the formation of traces of sulfur dioxide. N. Leonard (38) found that sublimed sulfur generally colors blue litmus red; and it contains 0.02 - 0.25% of sulfuric acid. Part of this acid is formed by exposure to air and moisture. Moist sublimed sulfur, free from acid, was distinctly acid after being kept for two weeks in a stoppered bottle, and after four years contained 0.2% of sulfuric acid and no sulfurous acid; a similar specimen, dried at 100°, contained only 0.0025% sulfuric acid after four years. A. G. Doroschevsky and G. S. Pavloff (39) observed that when charcoal is soaked in a solution of sulfur in carbon disulfide and dried, the sulfur undergoes oxidation at 100°.

W. Zanker and E. Farber (40) showed that powdered sulfur from different sources could not be freed of acid by washing, which would seem to indicate that the acid is continuously formed by the action of air and moisture. Flowers of sulfur contain the greatest amount of acid while colloidal sulfur is almost as strongly acid. The autoxida-
tion of sulfur occurs more readily in an acid than in a neutral or alkaline medium.

R. H. Simon and C. J. Schollenberger (41) observed that the rate of oxidation of sulfur in solution is dependent upon particle size. A. Harpf (42) also noticed that finely divided sulfur is oxidized on exposure to air in light or in darkness.

H. Moissan (43) found that oxidation occurs in sealed tubes with oxygen at 20°. The action is slower in air.

E. Pollacci (44) said that the oxidation of finely divided sulfur in air is accelerated by light; and that pure oxygen does not effect the oxidation. He claims that ozone is the active agent.

M. Bodenstein and W. Karo (45) found that the rate of oxidation was roughly proportional to the surface of the sulfur. It is, therefore, concluded that the reaction is a chemical one; that it occurs in the adsorption layer on the surface of the sulfur; and, that the sulfur dioxide which accumulates in the adsorption layer has no effect on the velocity of the reaction.

A. and P. Thenard (46) said that ozone oxidizes sulfur to sulfur dioxide; and A. Mailfert (47) observed that in the dry state only the dioxide, no trioxide, was formed while in the moist state only sulfuric acid is produced.

C. F. Cross and H. F. Higgin (43) found that sulfur begins to decompose water at about 95° in traces:

\[ \text{H}_2\text{O} + 3\text{S} \rightleftharpoons 2\text{H}_2\text{S} + \text{SO}_2 \]
At ordinary temperatures there is apparently no action.

According to S. Kitashima (49) free sulfur is not attacked by hydrochloric acid unless in the presence of iron.

G. N. Lewis (50) and co-workers found that when aqueous solutions of chlorates are heated with sulfur to 150-180°, they are slowly reduced; bromates are reduced to bromine, iodates to iodine; perchlorates and periodates are not acted on at 180°.

M. Raffo (51) and co-workers found that when iodic acid is mixed with sulfur, a deep red color due to free iodine is immediately developed, and subsequently a voluminous dark red precipitate composed of a mixture of iodine and sulfur separates. There is evidence that the sulfur is oxidized to sulfur dioxide by the iodic acid, the resulting hydriodic acid is oxidized to free iodine by part of the iodic acid, and the latter also oxidizes the sulfur dioxide to sulfuric acid. Under certain conditions, the reaction at first increases with the iodic acid concentration, attains a maximum and beyond that point diminishes, with further increase in concentration. According to the conditions, the reaction proceeds until the iodic acid or the sulfur is used up, or until the sulfur separates in a gelatinous form.

According to C. C. Palit and N. R. Dhar (52) 15 and 26% nitric acid have no action on sulfur at ordinary temperatures. H. Zieler (53) observed no reaction with nitric
acid up to 40% acid, and with boiling 50% acid only a feeble reaction occurred.

The action of alkali hydroxides on sulfur is discussed more fully under Thiosulfates. C. Fahlberg and M. W. Iles (54) said that when potassium hydroxide is fused with sulfur, sulfide and thiosulfate are formed; with an excess of alkali only sulfite and sulfate are formed. M. J. Fordos and A. Gelis (55) found that with boiling alkali and sulfur more thiosulfate is formed than corresponds with the equation:

\[ 3K_2O + nS + H_2O = 2K_2S_{n-2} + KS_2O_3 + H_2O \]

J. B. Senderens (56) said that the equation represents a limiting case applicable only to concentrated solutions; with dilute solutions, the polysulfide is decomposed into thiosulfate and hydrogen sulfide.

According to H. V. Tartar (57) the primary reaction of sulfur with potassium hydroxide in hot aqueous solution takes place in accordance with the equation:

\[ 6KOH + 3S = 2K_2S_3 + KS_2O_3 + 3H_2O \]

When sulfur is used in excess a secondary reaction occurs in which it combines with the trisulfide to form the pentasulfide. A variation of the temperature (below 100°) and concentration does not alter the nature of the reaction.

H. Pomeranz (58) supposed that some hydrosulfite was formed.

W. Selezneff (59) observed that alkali nitrates are
not decomposed when boiled with sulfur. A solution of potassium dichromate yields chromium chromate, potassium sulfite, and potassium sulfate.

E. Pollacci (60) said that hydrogen peroxide does not oxidize finely divided sulfur.

3. Sulfurous Acid

Sulfur dioxide is formed when sulfur is burned in oxygen or air. These vapors when led into water form sulfurous acid, H₂SO₃.

Also sulfur dioxide results as a product in many chemical reactions involving sulfur compounds. Only those taking place in aqueous solutions and which may have some possible connection with the problem at hand will be reviewed.

Sulfur dioxide is produced by the action of concentrated mineral acids on sulfites, thiosulfates, and all polythionic acids.

L. G. Wesson (61) found that solid metahydrosulfite alone or mixed with a dry solid pyrosulfate is hygroscopic in moist air, and gives off sulfur dioxide.

G. Neumann (62) obtained sulfur dioxide from a Kipp’s apparatus by using cubes made of calcium sulfite and plaster of Paris, and concentrated acid.

E. Geisel (63) and F. W. Kuster and F. Abegg (64) devised an apparatus for preparing the gas from concentrated sulfuric acid and a solution of hydrosulfite.
W. Garroway (65) decomposed a solution of sodium hydrosulfite by sodium hydrosulfate or sulfuric acid. Most of the sulfur dioxide is driven out in the cold, the remainder by the injection of steam.

P. Pierron (66) obtained sulfur dioxide at the anode during the electrolysis of ammonium thiosulfate.

A. Fischer and G. Delmarcel (67) studied the electrolytic oxidation of sulfurous acid, using a partitioned cell with sulfuric acid or sodium sulfate as catholyte, and sulfurous acid as anolyte, and a nickel or platinum cathode, and a cylinder of platinum gauze as anode. Better results are obtained with low than with high concentrations of the electrolytes. When oxygen begins to be liberated at the anode, there is a sudden drop in the current strength.

M. de K. and N. J. Thompson (68) observed that sulfurous acid is easily oxidized at platinum electrodes to sulfuric acid at any concentration below 95%. The primary products of electrolysis are hydrogen and oxygen, sulfur dioxide being a secondary product.

D. F. Smith and J. E. Mayer (69) calculated -0.138 volts for the reduction potential of

\[ \text{SO}_4^{2-} + 4H^+ = \text{SO}_3 + 2H_2O \]

and they gave -6350 calories for the decrease of free energy, at 25°. Comparing this result with the values for hydrogen sulfide it follows that the reducing powers of the two gases in molar solution are nearly equal; for
higher concentrations of hydrogen ion the reducing power of hydrogen sulfide is greater. Sulfur dioxide is a reducing agent in dilute acid solution and an oxidizing agent in concentrated acid solution.

In the cathode reduction of sulfur dioxide in acid solution, hydrogen sulfide is not formed as a primary product, and it is thought that hyposulfurous acid—or possibly thiosulfuric acid, thionic acid, or an active form of sulfur—is primarily formed.

A. A. Noyes and H. H. Steinour (70) found that the e.m.f., \( E \), of a platinised platinum electrode in a solution of sulfite ions and hydrogen ions, under quiet conditions, is fairly constant, but when the solution is agitated for a long time, \( E \) becomes negative and then gradually increases to the value for the quiescent state. The potential is not accidental; at 25°, it is given by \( E = -0.37 - 0.0296 \log(H^+)^{4/3} \); it is attributed to sulfurous acid, and a decomposition product of this acid. It is independent of the initial condition of the electrode, and is scarcely affected by the presence of sulfuric, hydrochloric or dithionic acid. It is supposed to be hyposulfurous acid, and the nearly constant value of \( E \) is said to be due to the rate of production of this acid from sulfurous acid, being equal to the rate at which it spontaneously decomposes. The addition of sulfur has no influence on \( E \) at low temperatures, but at higher temperatures, it may affect the potential because of the accelerated rate of decomposition.
of the hyposulfurous acid. The potential is complicated by the presence of oxygen, since this latter assists the decomposition of hyposulfurous acid.

The aqueous solution of sulfur dioxide is slowly oxidized in air, forming sulfuric acid, while, C. L. Reese (71) found that dilute solutions are rapidly oxidized.

J. Priestly (72) and others observed that when an aqueous solution of sulfur dioxide is heated some sulfur is formed.

F. Forster (73) and co-workers found that the autoxidation:

\[ 2\text{H}_2\text{SO}_3 = 2\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{S} \]

is complete only after several days at 100°. It is autocatalytic, being accelerated by the sulfur but retarded by the hydrogen ions formed. It is accelerated by the action of light. The mechanism of the change is complex, thiosulfuric and polythionic acids being formed as intermediate products.

F. Forster and co-workers consider that two different kinds of molecules must be present in the oxidation and reduction which is the first step in the process of autoxidation; they consider that these two different forms of \( \text{HSO}_3^- \) ions or of \( \text{S}_2\text{O}_8^{2-} \) ions react according to:

\[ 2\text{HSO}_3^- = \text{SO}_4^{2-} + \text{H}_2\text{SO}_4 \] (sulfoxylic acid)

or,

\[ \text{S}_2\text{O}_8^{2-} = \text{SO}_4^{2-} + \text{S} \] (sulfoxylic anhydride)

As indicated in connection with the action of light on a solution of sulfurous acid and the sulfites, it may
assumed that some pyrosulfurous acid is present in the solution of sulfurous acid, and accordingly, H. Bassett and R. G. Durrant (74) assume that the two kinds of molecules concerned in the first state of autoxidation are $\text{H}_2\text{SO}_3$ and $\text{H}_3\text{S}_2\text{O}_8$, and the reaction proceeds:

$$\text{H}_2\text{SO}_3 + \text{H}_3\text{S}_2\text{O}_8 \rightleftharpoons \text{H}_2\text{SO}_4 + \text{H}_2\text{S}_2\text{O}_4$$

where hyposulfurous acid is the most probable product in the first stage of the reduction of the pyrosulfurous acid. Owing to instability of this acid, proof is difficult, although E. Jungfleisch and L. Brunel (75) and F. Forster (73) observed that hyposulfurous acid is formed under some conditions.

Bassett and Durrant (74) said the only reaction for hyposulfite in sulfite solution undergoing autoxidation is the bleaching of indigo. They say that trithionic acid is the initial decomposition product of thiosulfuric acid:

$$2\text{H}_3\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{S}_3\text{O}_6$$

and this gradually yields tetrathionic and pentathionic acids as the concentration of the sulfurous acid diminishes with the progress of the autoxidation. The polythionic acids decompose in their turn, and the final products of the autoxidation are sulfur and sulfuric acid. On account of this polythionic acid formation during autoxidation, tri- and tetrathionic acids are almost always present in old sulfurous 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. No separation of sulfur
occurs for a long time, because the excess of sulfurous
acid stabilizes both the sulfoxylc and the thiosulfuric
acids by yielding with them the sulfur dioxide addition-
complexes. Formation of thiosulfate from sulfite and sul-
fur, according to the reaction:

$$\text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{SO}_3 + \text{S}$$

is greatly facilitated as well as the formation of tri-
thionate:

$$2\text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{S}_2\text{O}_4$$

The hydrogen sulfide is removed by interaction with sul-
foxylc acid:

$$\text{H}_2\text{S} + \text{S(OH)}_2 \rightleftharpoons 2\text{S} + 2\text{H}_2\text{O}$$

with pyrosulfuric acid:

$$\text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{S} \rightleftharpoons \text{S(OH)}_2 + \text{H}_2\text{O} \cdot \text{S}_2\text{O}_3$$

or with sulfur dioxide of the complex \(\text{H}_2\text{S}_2\text{O}_4(\text{SO}_3)\)\:

$$\text{H}_2\text{S} + (\text{SO}_3) = \text{S} + \text{S(OH)}_2$$

While the thiosulfate is formed during the autoxida-
tion of sulfurous acid, the acidity or hydrogen ion
concentration increases, and the addition of acid is un-
favorable to the reaction. On this account pyrosulfite
solutions undergo autoxidation much more rapidly than sul-
furous acid solutions. This effect of the hydrogen ion is
connected with its effect in the equilibria:

$$\text{H}^+ + \text{HSO}_3^- \rightleftharpoons \text{H}_2\text{SO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_3$$

The more acid the solution the more sulfur dioxide we have
present, and since the autoxidation becomes correspondingly slower, this favors the view that sulfur dioxide is one of the primary reactants.

Various liquids other than water were shown by E. Matthews (76) to favor the reaction of hydrogen sulfide with sulfur dioxide; and the assumption that pyrosulfurous acid is one of the primary products of the reaction is supported by G. M. Bennett's (77) observation that sulfur, or even hydrogen sulfide, was liberated when sodium sulfite or pyrosulfite in the solid state or in a saturated solution, was added to hot concentrated sulfuric or phosphoric acid. Sulfur dioxide or its saturated solution in water do not act this way. In conclusion, H. Bassett and R. G. Burstant (78) added that the reduction of sulfulorous acid in aqueous solution probably proceeds normally to hyposulfite, and not directly to sulfur or hydrogen sulfide. These substances are products of the reduction of hyposulfurous, sulfoxylic, or thiosulfuric acid.

F. Forster (79) showed that the spontaneous decomposition of sulfulorous acid is autocatalytic, and is accelerated by the presence of selenium. The first products of the reaction are sulfuric and trithionic acids, but not tetra-thionic acid:

\[ 4\text{HSO}_3^- = \text{SO}_4^{2-} + \text{S}_2\text{O}_6^{2-} + \text{H}_2\text{SO}_3 \]

The slower the reaction the greater the decomposition of the trithionate according to the equation:

\[ \text{S}_2\text{O}_6^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{S}_2\text{O}_5^{2-} + 2\text{H}^+ \]
The autocatalytic nature of the main reaction is ascribed to the hydrogen ion whose concentration increases more rapidly than is shown by methyl orange titration due to the disappearance of the bisulfite ion. The mechanism of the process is as follows: The seleno-dithionate ion formed rapidly by the action of hydrogen sulfite solution on selenium or on selenious acid, undergoes decomposition, accelerated by the hydrogen ion:

\[ \text{SeS}_2\text{O}_6^{2-} + \text{H}_2\text{O} = \text{SO}_4^{2-} + \text{SeS}_2\text{O}_3^{2-} + 2\text{H}^+ \]

In the presence of hydrogen sulfite ions a series of reactions takes place:

\[ \text{SeS}_2\text{O}_6^{2-} + 2\text{H}^+ \rightleftharpoons \text{SeO} + \text{SO}_2 + \text{H}_2\text{O} \]
\[ \text{SeO} + 2\text{H}_2\text{SO}_3^- = \text{SeS}_2\text{O}_6^{2-} + \text{H}_2\text{O} \]
\[ \text{SO}_2 + 2\text{H}_2\text{SO}_3^- = \text{S}_2\text{O}_6^{2-} + \text{H}_2\text{O} \]

In the absence of selenium, the hydrogen sulfite ion decomposes very slowly, according to the equation:

\[ 4\text{H}_2\text{SO}_3^- = 2\text{SO}_4^{2-} + \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \]

The resulting hydrogen ions in this case also effect autocatalysis, probably through the formation of polythionates.

L. J. Thenard (80) and J. Meyer (81) found that hydrogen peroxide oxidizes sulfurous acid and sulfites to sulfates; and A. Nabl (82) represented the reaction:

\[ 2\text{H}_2\text{SO}_3 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{H}_2\text{S}_2\text{O}_6 \]

followed by:

\[ \text{H}_2\text{S}_2\text{O}_6 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{SO}_4 \]
F. Forster (83) said that the reaction:

(a) \( 3\text{H}_2\text{SO}_4 \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+ + \text{S} + \text{H}_2\text{O} \)

is very slow requiring many days for completion at 100° and two days at 150°. The mechanism is as follows where reaction (b) is by far the slowest:

(b) \( 2\text{HSO}_4^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{S} \)

(c) \( 2\text{SO}_4 = \text{S}_2\text{O}_3^2- + \text{H}_2\text{O} \)

(d) \( \text{HSO}_4^- + \text{S} \rightarrow \text{S}_2\text{O}_3^2- + \text{H}^+ \)

(e) \( 5\text{S}_2\text{O}_3^2- + 6\text{H}^+ \rightarrow 2\text{S}_2\text{O}_5^2- + 3\text{H}_2\text{O} \)

(f) \( \text{S}_2\text{O}_3^2- + \text{HSO}_4^- \rightarrow \text{S}_2\text{O}_5^2- + 2\text{H}_2\text{O} + \text{H}^+ \)

(g) \( \text{S}_2\text{O}_3^2- + \text{HSO}_4^- \rightarrow \text{S}_2\text{O}_5^2- + \text{S}_2\text{O}_3^2- + \text{H}^+ \)

(h) \( \text{S}_2\text{O}_3^2- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_3^2- + 2\text{H}^+ \)

B. Neumann and F. Wilczynski (84) represented the reaction of moist sulfur dioxide with chlorine as follows:

\( \text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4 + 2\text{HCl} \)

In aqueous solution:

\( \text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{H}_2\text{SO}_4 \)

C. Mayr and J. Peyfuss (85) represented the reaction with bromine:

\( \text{SO}_2 + 2\text{H}_2\text{O} + \text{Br}_2 \rightarrow 2\text{HBr} + \text{H}_2\text{SO}_4 \)

According to R. Bunsen (36) the oxidation of sulfurous acid by iodine is complete:

\( 2\text{SO}_2 + 4\text{H}_2\text{O} + 2\text{I}_2 \rightarrow 2\text{H}_2\text{SO}_4 + 4\text{HI} \)

provided the solution contains less than 0.04% acid.

According to J. Volhard (87):

\( \text{SO}_2 + 4\text{HI} = 2\text{H}_2\text{O} + 2\text{I}_2 + \text{S} \)

\( 2\text{SO}_3 + 4\text{H}_2\text{O} + 4\text{I} \rightarrow 2\text{H}_2\text{SO}_4 + 4\text{HI} \)
The action of hydrosulfites and iodine:

\[ 2\text{NaHSO}_3 + \text{I}_2 + 2\text{H}_2\text{O} = 2\text{NaHSO}_4 + 4\text{HI} \]

was studied by R. Bunsen, M. J. Fordos and A. Gelis (89) and others.

E. Sokotoff and P. L. Maltschewsky (90) said that some dithionous acid is formed:

\[ 2\text{NaHSO}_3 + \text{I}_2 = 2\text{NaI} + \text{H}_2\text{S}_2\text{O}_3 \]

R. Otto and J. Troger (91) represented the reaction with a mixture of sulfides and sulfites by the equations:

\[ \text{Na}_2\text{S} + \text{I} = 2\text{NaI} + \text{S} \]

\[ \text{Na}_2\text{SO}_3 + \text{S} = \text{Na}_2\text{S}_2\text{O}_3 \]

W. Feit and C. Kubierschky (92) found that bromic acid completely oxidizes sulfurous acid to sulfuric acid.

The action of bromates was studied by W. S. Hendrixson (93) and he attributed the incompleteness of the reaction in acid solution to some dithionate.

Sulfur dioxide and sulfurous acid do not react with sulfur, although H. Debus (94) said that with sulfurous acid an insignificant amount of pentathionic acid was formed; and A. Colfax (95) found that in darkness and at ordinary temperatures, and more rapidly at elevated temperatures, we have the formation of not pentathionic acid, but rather di-, tri-, or tetrathionic acid.

J. Swingle and T. Morawsky (96) found that hydrogen sulfide decomposes sulfurous acid yielding pentathionic
acid and sulfur, while W. Spring (97) and H. Hertlein (98) noted the formation of sulfur, tetrathionic, and dithionite acids.

H. Ritter (99) observed that will alkali sulfides, sulfates are produced; and J. Volhard (100) that sulfur, sulfate and hyposulfite are formed. E. Divers and T. Shimizu (101) found that with hydrosulfides thiosulfates are produced.

R. Weber (102) found that nitrous acid oxidizes sulfurous acid at ordinary temperatures to sulfuric acid.

Aqueous solutions of nitric acid and sulfurous acid do not react at ordinary temperatures according to F. Raschig (103).

W. S. Hendrixson (104) studied the reducing action of sulfurous acid on dichromates which is incomplete in acid solution due to the formation of some dithionate.

Alkaline solutions of sulfur dioxide were found by F. Heeren (105), L. P. de St. Gilles (106), M. J. Fordos and A. Gelis (107), and J. H. Buignet (108) to be almost completely oxidized to sulfate by permanganate but in acid solution about one-fifth goes to dithionite acid.

T. S. Dymond and F. Hughes (109) said the reaction is:

$$17\text{H}_2\text{SO}_3 + 6\text{KMnO}_4 = 2\text{K}_2\text{S}_2\text{O}_8 + \text{K}_2\text{SO}_4 + 6\text{MnSO}_4 + 6\text{H}_2\text{SO}_4 + 11\text{H}_2\text{O}$$

If sulfurous acid is introduced into an excess of permanganate, sulfuric acid alone is produced.

The oxidation of solutions of sodium sulfite in air
is greater the less the concentration of the salt. A 80% solution is negligibly oxidized by exposure to air. S. L. Bigelow (110) also noticed that the curves representing the concentration of the solution with time are straight lines until a concentration of 0.002N sodium sulfite is reached when they rapidly bend down showing a marked decrease in the speed of oxidation. This is explained by assuming that the velocity constant of the reaction is large, so that until the concentration of the solution is small, oxygen is removed from the solution faster than it is absorbed.

According to E. H. Riesenfeld and T. F. Egidius (111), a neutral solution of sodium sulfite reacts with ozone, forming sulfate and dithionate.

A. Longi and L. Bonavia (112) found sodium dioxide readily oxidizes sulfites quantitatively to sulfate.

4. Sulfuric Acid

Sulfur trioxide, \( \text{SO}_3 \), the anhydride of sulfuric acid is produced to the extent of about two percent in the ordinary combustion of sulfur. The equilibrium

\[ 2 \text{SO}_3 + \text{O}_2 \rightleftharpoons 2\text{SO}_2 \]

can be shifted almost completely to the right by use of a catalyst under the proper conditions.

However, in this work we are not interested in the reactions of the dry gas but rather in reactions which occur in aqueous solution which give rise to sulfuric acid.
The review of the literature was carried out with this idea in mind.

E. Becquerel (113) stated that sulfuric acid could be produced by the action of various oxidizing agents—chlorine, hypochlorous acid, nitric acid, and a mixture of nitric acid and potassium chlorate—on sulfur.

The formation of sulfuric acid by the oxidation of sulfur dioxide by hydrogen peroxide, the halogens, hypochlorous acid, nitric acid, and by many salts of the metals, has been discussed under Sulfurous Acid.

Commercial processes have been suggested for oxidizing sulfur dioxide with chlorine to produce hydrochloric and sulfuric acids simultaneously:

\[ \text{SO}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 = \text{H}_2\text{SO}_4 + 2\text{HCl} \]

e.g. W. Haehner (114), H. Tobler (115), and A. Coppadoro (116).

B. Neumann and F. Wilczewsky (117) obtained sulfuric acid and hydrochloric acid from sulfurous acid and chlorine.

Sulfuric acid is formed by the action of oxidizing agents on the polythionic acids and on thiosulfuric acids or thiosulfates. E. F. Smith (118) obtained sulfuric acid as a product of the electrooxidation of metal sulfides.

According to A. von Bayer and V. Villiger (119), hydrogen dioxide reacts with concentrated sulfuric acid, forming permonosulfuric acid, \( \text{H}_2\text{SO}_8 \); and T. M. Lowry and J. N. West (120) studied the equilibrium conditions of the reactions:

\[ \text{H}_2\text{O}_8 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{SO}_8 + \text{H}_2\text{O} \]
and \[ \text{H}_2\text{O}_2 + 2\text{H}_2\text{SO}_4 = \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} \]

M. Berthelot (121) stated that the reaction would not take place if the sulfuric acid contained two equivalents of water or more.

J. L. Gay Lussac (122) and J. Kolb (123) stated that the hypochlorites are decomposed by sulfuric acid, forming hypochlorous and hydrochloric acids, and some chlorine through the decomposition of the hypochlorous acid.

F. von Stadion (124) and G. S. Serullas (125) said that the perchlorates are not decomposed at temperatures below 100° by concentrated sulfuric acid.

F. C. Vogel (126) showed that when concentrated sulfuric acid is heated with sulfur, sulfur dioxide is formed. R. H. Adie (127) observed that sulfur dioxide appears at 200°, and no hydrogen sulfide is formed.

F. C. Vogel (126) said that when hydrogen sulfide is passed into sulfuric acid, water is formed as well as some sulfurous acid and sulfur, but when the acid is diluted with four volumes of water, no reduction occurs.

According to A. P. deFourcroy and L. N. Vauquelin (128), when sulfur dioxide is passed into well-cooled sulfuric acid, no hyposulfurous acid is formed, but the frozen mass evolves sulfur dioxide when thawed.

5. Thiosulfuric Acid

According to C. F. Rammelsberg (129) and E. Divers and M. Ogawa (130) when a solution of calcium thiosulfate--
obtained by boiling lime and sulfur together with water, and leaving the solution until much of the pentasulfide has oxidized—is treated with an excess of ammonium carbonate, filtered, and freely exposed to air for some time at 50-60°, a concentrated solution of ammonium thiosulfate is obtained, free from sulfate and other salts.

E. Divers and M. Ogawa (131) found that the salt decomposes very slowly at 150°, the main products being a sublimate of anhydrous normal sulfite and a residue of unfused sulfur.

According to P. Pierron (132), when ammonium thiosulfate is electrolyzed in a compartment cell, with a platinum cathode and lead anode, below 15°, ammonium sulfide is the only product obtained at the cathode, while at the anode, sulfur, with various proportions of sulfurous, sulfuric, trithionic, and tetrathionic acids is formed. The amounts of sulfur and sulfuric acid increase while that of tetrathionic acid decreases as the current density rises from 10 to 40 amperes per square decimeter.

F. Chaussier (133) prepared sodium thiosulfate, Na₂S₂O₃—which he called hydrosulfure sulfure de soude—from sulfurous acid and sodium sulfide, or from sodium sulfite and hydrogen sulfide. L. N. Vauquelin (134) prepared what he called sulfites sulfures, by digesting a solution of sodium sulfate or sulfite with sulfur; and J. F. W. Herschel (135) called the salt hyposulfite of soda, and obtained it by oxidizing a solution of calcium
hydrosulfide in air, and subsequent double decomposition with a sodium salt. The salt is produced by the action of sulfur on the alkali hydroxide or carbonate, or by the action of sulfur on the hydroxides or carbonates of the alkaline earths and subsequently transforming, e.g. calcium thiosulfate into the sodium salt by double decomposition with alkali sulfate and crystallization.

M. J. Fordos and A. Gelis (136) showed that rather more thiosulfate is formed than corresponds with the reaction:

\[ 3 \text{Na}_2\text{O} + \text{nS} + \text{H}_2\text{O} = 2\text{Na}_2\text{S}_\text{n-2} + \text{Na}_2\text{S}_\text{n} + \text{H}_2\text{O} \]

O. J. B. Senderens (137) said that this reaction applies only to a limiting state when the solutions are sufficiently concentrated to allow the formation of a high polysulfide; with dilute solutions, the polysulfide forms thiosulfate and hydrogen sulfide. The reaction with alkali carbonate can be symbolized:

\[ 3 \text{Na}_2\text{CO}_3 + \text{nS} = \text{Na}_2\text{S}_\text{n} + 2\text{Na}_2\text{S}_\text{n-3} + 3\text{CO}_2 \]

and with milk of lime:

\[ \text{Ca(OH)}_2 + \text{S} = \text{CaS} + \text{H}_2\text{O} + \text{O} \]
\[ \text{CaS} + 3\text{O} = \text{CaSO}_3 \]
\[ \text{CaSO}_3 + \text{S} = \text{CaS}_2\text{O}_3 \]
\[ \text{CaS} + 4\text{S} = \text{CaS}_4 \]

H. Pomeranz (138) supposed that the reaction results in the formation of sulfoxalate:

\[ 4\text{NaOH} + 2\text{S} = \text{Na}_2\text{S} + \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O} \]

or

\[ 3\text{NaOH} + 2\text{S} = \text{Na}_2\text{S} + \text{NaHSO}_3 + \text{H}_2\text{O} \]

C. Fahlberg and M. W. Iles (139) said that the molten
alkali hydroxide, if not in excess, reacts with sulfur to form polysulfide and thiosulfate, but if in excess, alkali sulfite and sulfate.

Thiosulfate is also produced by the action of sulfur on alkali or alkaline earth sulfates, phosphates, or chromates. Thus, T. Salser (140) gave:

\[ nNa_4P_2O_7 + 12S + 3H_2O = 2Na_2S_8 + Na_2S_2O_3 + 6Na_2HP_2O_7 + (n-6)Na_4P_2O_7 \]

Thiosulfates are produced by the action of hydrogen sulfide or alkali sulfides on sulfur dioxide or sulfites. Thus, L. M. Vauquelin (141) showed that:

\[ 2Na_2S + 3SO_2 = 2Na_2S_2O_3 + S \]

and E. Drechsel (142):

\[ Na_2S_2O_3 + 2NaSH = Na_2SO_4 + Na_2S_2O_3 + H_2S \]

the Chemische Fabrik Griesheim-Electron (143):

\[ 2NaHSO_3 + 2Na_2S + 2SO_2 = 3Na_2SO_3 + H_2O \]

F. Raschig (144) represented the reaction:

\[ 6NaHSO_3 + 2Na_2S + 2SO_2 = 2Na_2SO_3 + 3Na_2S_2O_3 + 3H_2O \]

F. Forster (145) showed that:

\[ H_2S + H_2SO_3 \rightleftharpoons H_2S_2O_3 + H_2O \]

where the intermediate product is converted by an excess of sulfuric acid into sulfoxylic acid which becomes polymerized to thiosulfuric acid:

\[ H_2S_2O_3 + H_2SO_3 + H_2O = 3H_2SO_3 \]

and \[ 2H_2SO_3 = H_2S_2O_3 + H_2O \]

The production of thiosulfuric acid may, therefore, be expected to be the end point of the changes if the
reaction can be conducted under conditions such that the hydrogen ion concentration is insufficient to affect the stability of the thiosulfate ion. These conditions are realized experimentally when an aqueous solution of sodium hydrosulfide and sodium hydrosulfite in the molecular proportions 1:2 are mixed, whereby sodium thiosulfate is obtained directly and in a high degree of purity:

$$2\text{NaHS} + 4\text{NaHSO}_3 = 3\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$$

The preparation of sodium thiosulfate from sodium sulfide and sulfur dioxide or from sodium sulfite and hydrogen sulfide occurs very smoothly and almost without separation of sulfur when alkali hydroxide is added initially to the solution in such amount as to lead ultimately to the presence of NaHS and NaHSO$_3$ in the correct proportions.

H. Bassett and R. G. Durrant (146) added that the synthesis of the thiosulfate here involves the consecutive reactions:

$$\text{H}_2\text{S} + \text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$$

$$\text{H}_2\text{S} + (\text{OH})_2\text{S} \rightleftharpoons 2\text{S} + 2\text{H}_2\text{O}$$

$$\text{S} + 2\text{H}_2\text{SO}_3 \rightleftharpoons \text{H}_2\text{S}_2\text{O}_3$$

Alkali favors the thiosulfate formation in the last reaction. Hence, in alkaline solution both thiosulfate and a mixture of sulfide and sulfite are equally stable. Only in the neighborhood of the neutral point is a synthesis of thiosulfate possible by this method. Sulfide and sulfite do not react in alkaline solution.

L. A. Buchner (147) also showed that hydrogen sulfide
or an alkali sulfide may furnish thiosulfate by reacting with boiling solutions of different alkali salts in air—e.g. borates, chlorates, acetates, tartrates, and phosphates; and G. Chancel and E. Diacon (148) show that with tetrathionates:

$$\text{Na}_2\text{S} + \text{Na}_2\text{S}_4\text{O}_6 = \text{S} + 2\text{Na}_2\text{S}_3\text{O}_3$$

Thiosulfates are also formed by the oxidation of solutions of sulfides or polysulfides. Thus, in the electrolysis of a solution of sodium sulfide or sodium hydro-sulfide, F. W. Durkee (149) observed that the thiosulfate is formed as an intermediate product of the oxidation of sulfides to sulfates. During the electrolysis of a dilute solution of sodium sulfide (containing about 3.4 grams of sodium in 400 cc.) by a current of about three amperes, hydrogen was evolved at the cathode, and the liquid became yellow, at first around the cathode and ultimately throughout; light yellow sulfur then appeared on the anode, but scaled off again, and in greater part dissolved; fine white sulfur next separated near the surface of the liquid about the anode, but dissolved as it sank through the solution until a certain stage of the electrolysis, when the yellow color of the liquid disappeared and the white sulfur settled in the beaker; subsequently more oxygen escaped than at any other previous stage. The separation of white sulfur is characteristic of the oxidation of thiosulfate while the appearance of yellow sulfur is incidental to the presence of polysulfide. These facts indicate that the
course of the oxidation of sodium sulfide by electrolysis is similar to that of its oxidation by air; the sulfide is first oxidized to hydroxide and thiosulfate, the latter passing to sulfate with separation of sulfur; this sulfur dissolves in unaltered sulfide to form polysulfides which are oxidized to thiosulfate with separation of sulfur. Thus, during electrolysis, sulfides disappear first, then the hydroxide and finally the thiosulfate, the sulfate being virtually the end product. On electrolyzing sodium sulfide with alternating current the platinum electrodes dissolved, whereas, no such dissolution was noticed with direct current electrolysis.

A. Scheurer-Kestner (150) holds that the sulfide is oxidized direct to sulfate without the intermediate formation of thiosulfate.

6. Lunge (151) and co-workers have studied the oxidation of sodium sulfide in air. There are two stages in the process. In dilute solutions the oxidation even in boiling liquor, does not proceed beyond thiosulfate:

\[ 2\text{Na}_2\text{S} + \text{O}_2 + \text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH} \]

As the liquor becomes concentrated the thiosulfate is reduced to sulfide and sulfite, and no sulfate is formed:

\[ 3\text{Na}_2\text{S}_2\text{O}_3 + 6\text{NaOH} = 2\text{Na}_2\text{S} + 4\text{Na}_2\text{SO}_3 + 3\text{H}_2\text{O} \]

If the alkali sulfide be fused, air may oxidize the sulfide to sulfite and finally to sulfate. If alkali nitrate is present there is no reaction below 138°;
above 138°:
\[ \text{Na}_2\text{S} + 2\text{NaNO}_3 = 2\text{NaNO}_2 + \text{Na}_2\text{SO}_3 \]

at 180-192°:
\[ \text{Na}_2\text{S} + 4\text{NaNO}_3 = \text{Na}_2\text{SO}_4 + 4\text{NaNO}_2 \]

Iron catalyzes the reaction below 138°.

E. E. Naef (158) found that the oxidation of powdered hydrated sodium sulfide proceeds at ordinary temperature in the presence of finely divided active charcoal.

H. C. Jones (155) showed that alkali polysulfides form thiosulfate by atmospheric oxidation:
\[ 2\text{Na}_2\text{S}_x + 3\text{O}_2 = 2\text{Na}_2\text{S}_2\text{O}_3 + 6\text{S} \]

P. de Clermont and J. Frommel (154), P. Kircheisen (155), V. Legrip (158), A. Colson (157) and E. Drechsel (158) obtained the thiosulfate by boiling the aqueous solution:
\[ 2\text{Na}_2\text{S}_x + 3\text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{S} \]

H. Brunner (159) by treatment with sodium nitrate; W. Spring (160) by oxidation with iodine:
\[ \text{Na}_2\text{S} + \text{Na}_2\text{SO}_3 + \text{I}_2 = \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaI} \]

K. W. Jurisch (161), P. Pauli (162), E. Carey (163), R. Powell and W. Atkins (164), and E. Donath and F. Mullner (165) by oxidation with manganese dioxide:
\[ 2\text{Na}_2\text{S} + 8\text{MnO}_2 + \text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH} + 4\text{Mn}_2\text{O}_3 \]

or with dichromates:
\[ 2\text{Na}_2\text{S}_x + 4\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} = 5\text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH} + 4\text{Cr}_2\text{O}_3 \]

Thiosulfates are produced by the union of sulfur with sulfites. Thus, by boiling an aqueous solution of a sulfite
with sulfur:
\[ \text{Na}_2\text{SO}_3 + S = \text{Na}_2\text{S}_2\text{O}_3 \]

H. Bassett and R. G. Durrant (166) showed that the reaction is reversible but the thiosulfate is very stable in alkaline solution so that thiosulfate is readily formed by boiling alkaline sulfite solution with sulfur. Nevertheless, even in alkaline solution there may be a perfectly definite, although very small, dissociation into sulfite and sulfur. If alkaline thiosulfate solutions containing alkali sulfide are boiled in the absence of air, they become deep yellow owing to the formation of polysulfide, the extra sulfur for which is obtained from the thiosulfate.

The equilibrium between sulfide and thiosulfate may be written:

\[ \text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{Na}_2\text{S}_2 + \text{Na}_2\text{SO}_3 \]

although higher polysulfides might result as well. Such a reaction does not necessarily involve a dissociation of thiosulfate into sulfur and thiosulfate. There can be little doubt that it is because of such an equilibrium that a trace of hydrogen sulfide greatly accelerates the reaction between sodium sulfide and sulfur.

The Verein chemischer Fabriken (167) prepared it by the reaction of sulfur dioxide on a mixture of alkali hydro-carbonate and S. G. Halphen (168) produced thiosulfate by electrolyzing an alkali sulfite; M. G. Levi and M. Voghera (169) worked at 25° with a concentrated solution of sodium sulfide in the cathode compartment, and a
feebly alkaline but concentrated solution of sodium sulfite in the anode compartment.

Thiosulfates are also formed by the decomposition of an aqueous solution of amid sulfites, hydrosulfites, trithionates, tetrathionates, and pentathionates.

According to J. L. Gay Lussac (170) aqueous solutions of the thiosulfates remain unchanged when exposed to air, but if over two mols of potassium hydroxide are present per mol of thiosulfate, oxidation occurs:

$$K_2S_2O_3 + 2KOH + O_2 = 2K_2SO_4 + H_2O$$

The solution is more stable if light be excluded.

W. Petzold (171) found that in the presence of acids, thiosulfates are first polymerized to pentathionates:

$$5S_2O_3^2- + 10H^+ = 2S_5O_6^{2-} + 4H^+ + 3H_2O$$

but thiosulfate may be regarded as an end product in the decomposition of aqueous solutions of the polythionates, i.e. the tri-, tetra-, and pentathionates.

According to J. Davidsohn (172) solutions of thiosulfates slowly decompose on standing exposed to air. The addition of alkali substances prevents the decomposition almost completely. The accelerative effect of deposited sulfur on the decomposition is probably due to bacterial action. The decomposition may be retarded by the addition of 0.01 gram of mercuric iodide per liter of solution.

F. L. Hahn and H. Windisch (173) said that the addition of a very small amount of alkali enables thiosulfate solutions to be preserved from the first day without
alteration. The change they otherwise undergo appears to be due to the faintly acid character of distilled water. According to A. Skrabel (174), a 0.1 N solution of sodium thiosulfate having a pH between 5 and 6 decomposed 1.28% after five months while one with pH of 9-10 had not changed. Solutions of greater acidity than this did not attain a constant titre at any time during the tests, and in the case of solutions of pH 5-6 sulfur separated during the first few weeks and was then gradually dissolved. Both hydrogen sulfide and sulfur dioxide could be detected in these solutions so they probably contained polythionic acids.

M. and M. L. Kilpatrick (175) found that freshly boiled, redistilled water yields a solution of thiosulfate that is more stable than a solution made with ordinary laboratory distilled water, or redistilled water through which carbon dioxide free air has been bubbled.

N. N. Mittra and N. R. Dhar (176) found that in the simultaneous oxidation of sodium sulfite (primary reaction) and thiosulfate (secondary reaction), the speed of the primary reaction is reduced.

According to W. Gluud (177), at 100°, in contact with air and under ten atmospheres pressure, sodium thiosulfate undergoes total transformation into sulfate, provided that sufficient alkali is present to unite with the sulfuric acid formed from the sulfur; if such excess of alkali is lacking, part of the sulfur separates in a
free state. A lower pressure may be used but in this case we must have a higher temperature or increase the time of the experiment.

C. Mayr (178) found that the prolonged passage of a current of pure air or of pure carbon dioxide or a mixture of both through thiosulfate solutions prepared from freshly boiled water causes no change in the titre, but exposure of the same solution to ordinary air soon results in the deposition of sulfur, and first a slight increase, then a more rapid decrease in the titre. This has been proven to be due to the inoculation of the solution with sulfur bacteria from the air; in the presence of carbon dioxide, the bacteria thrive to a limited extent and cause first the decomposition of thiosulfate to sulfite and sulfur and the subsequent oxidation of sulfite to sulfate.

C. F. Capaun (179) found that when water and thiosulfate are heated in a sealed tube, sulfur and sodium sulfite are formed; if air be present sulfate is formed.

E. H. Riesenfield and T. F. Egidius (180) observed that neutral solutions of thiosulfate react with ozone, forming sulfite and dithionate, but alkaline solutions give off oxygen so that two atoms of the ozone are active.

According to A. Nabl (181) the reaction of aqueous solutions of sodium thiosulfate with hydrogen peroxide can be represented:

$$2Na_2S_2O_3 + H_2O_2 = Na_2S_4O_6 + 2NaOH$$

provided the alkali hydroxide be neutralized as fast as it
is formed, otherwise tetrathionate is decomposed:

$$2Na_2S_2O_3 + 7H_2O_2 = 2Na_2SO_4 + H_2S_2O_6 + 6H_2O$$

and the dithionite acid is converted to sulfuric acid:

$$H_2S_2O_6 + H_2O_2 = 2H_2SO_4$$

R. Willstätter (182) observed that, if sodium thio-

sulfate and hydrogen peroxide are in the molar proportions

1:2, a mixture of sulfate and thionite is formed:

$$3Na_2S_2O_3 + 4H_2O_2 = 2Na_2S_3O_6 + 2NaOH + 3H_2O$$

and

$$Na_2S_2O_3 + 2NaOH + 4H_2O_2 = 2Na_2SO_4 + 5H_2O$$

He observed no tetrathionate.

A Casolari (183) represented the reaction:

$$Na_2S_2O_3 + 4H_2O_2 + H_2O = Na_2SO_4 + H_2SO_4 + 4H_2O$$

If the hydrogen peroxide be quite neutral, no alkalinity

with phenolphthalein appears but with methyl orange an

alkalinity corresponding to:

$$2Na_2S_2O_3 + H_2O_2 = 2NaOH + S_2O_3$$

develops. There is then a further reaction represented in

the cold probably by:

$$4S_2O_3 + 5H_2O_2 = H_2S_4O_6 + 4H_2SO_4$$

which is in accord with Nabl's (181) result above; and

in hot solution by:

$$4S_2O_3 + 5H_2O_2 = H_2S_3O_6 + 4H_2SO_4 + S$$

which agrees with Willstätter's (182) results.

The less energetic oxidizing agents convert thio-
sulfates to tetrathionates, e.g. hydrogen peroxide, iodine,
potassium iodate, cuprous chloride, and selenious acid.

G. Jorgansen (184) and M. J. Fordos and A. Gellis (185)
observed that chlorine and bromine oxidize thiosulfates to sulfates:

\[ \text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 3\text{HCl} \]

G. Lunge (186) said that the main reaction proceeds:

\[ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{Cl}_2 = 2\text{NaCl} + \text{Na}_2\text{S}_4\text{O}_6 \]

although some reacts in accord with M. J. Fordos and A. Gelis' equation; and possibly also:

\[ \text{Na}_2\text{S}_2\text{O}_3 + \text{Cl}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HCl} + \text{S} \]

C. Mayr and J. Peyfuss (187) represented the reaction with bromine in alkaline solution:

\[ \text{Na}_2\text{S}_2\text{O}_3 + 4\text{Br}_2 + 5\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 3\text{HBr} \]

In alkaline solution with chlorine or bromine it is probable that a hypochlorite or hypobromite is formed, and according to G. Lunge (186) when the thiosulfate is present in excess, the liquid becomes acid, and some hydrogen sulfide is formed presumably due to the reaction:

\[ 2\text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{S}_3\text{O}_6 + \text{Na}_2\text{S} \]

followed by the decomposition of the sulfide by acid and some hydrogen sulfide is evolved.

F. Raschig (188) said that sodium hypochlorite oxidized thiosulfate in acidic solution giving partly sulfate and partly thionate.

A. W. Francis (189) found the velocity constant for the oxidation of sodium thiosulfate with bromine to be 15.

F. Dienert and F. Wanderbulcke (190) found that in dilute solutions the reaction proceeds:

\[ 3\text{Na}_2\text{S}_2\text{O}_3 + 5\text{Cl}_2 + 5\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 3\text{HCl} + \text{H}_2\text{SO}_4 + \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaCl} \]
or \( 5\text{NaOCl} + 3\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O} = 2\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_4\text{O}_6 + 5\text{NaCl} \)
\[ + 5\text{H}_2\text{O} \]

In the presence of acids, however, or even in the presence of sodium bicarbonate, much less sodium thiosulfate is required, the reaction being:

\[ \text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} = 2\text{NaHSO}_4 + 8\text{HCl} \]

Hydrochloric acid reacts as follows:

\[ \text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} = \text{SO}_2 + \text{S} + 2\text{NaCl} + \text{H}_2\text{O} \]

with the intermediate formation of polythionates.

According to L. L. de Koinick (191) hypiodites oxidize thiosulfates as is the case with hypochlorites:

\[ 4\text{NaOI} + \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{NaHSO}_4 + 4\text{NaI} \]

W. Spring (192) and M. J. Fordos and A. Celis (193) found that chloric acid, or an acidified solution of potassium chlorate oxidize thiosulfates to tetrathionates.

W. Feit and K. Kubierschky (194) said that an acid solution of potassium bromate or bromic acid completely oxidizes thiosulfates in acidic solution to sulfuric acid and water.

A. Casolari (195) represented the reaction:

\[ \text{KBrO}_3 + 6\text{H}_2\text{S}_2\text{O}_3 = \text{HBr} + 3\text{H}_2\text{S}_4\text{O}_6 + 3\text{H}_2\text{O} \]

C. S. Jamieson (196) showed:

\[ \text{Na}_2\text{S}_2\text{O}_3 + 2\text{KIO}_3 + 2\text{HCl} = \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 2\text{ICl} + \text{H}_2\text{O} \]

When hydrogen sulfide is passed into a solution of sodium thiosulfate, sulfur is precipitated, slowly at ordinary temperatures but more quickly on warming. W. Petzold (197) gave the reaction as:
According to H. Bassett and R. G. Durrant (198) the sulfur is produced by the decomposition of thiosulfate:

\[
2H^+ + S_2O_3^{2-} \rightarrow 2H_2S + 2H_2O + S
\]

According to H. Debus (199) when potassium thiosulfate is dissolved in an excess of concentrated sulfuric acid, the intense yellow solution can be kept without apparent change. It can be shown that the products are sulfite and unchanged thiosulfate.

By use of a less concentrated solution of sulfuric acid, we find a different result. It is inferred that sulfuric acid decomposes a portion of the potassium thiosulfate forming sulfite and thiosulfuric acid which by condensation is transformed into pentathionic acid. Part of the thiosulfuric acid decomposes into sulfur and sulfuric acid. Potassium sulfite and pentathionate form thiosulfate and trithionate. Hence, potassium trithionate is the chief product:

\[
6K_2S_2O_3 + 96O_2 = K_2S_2O_6 + K_2S_4O_6 + 4K_2S_3O_6
\]

H. Hertlein (200) obtained a quantitative conversion of thiosulfate into trithionate by the action of concentrated sulfuric acid on a saturated solution of potassium thiosulfate at 80°C:

\[
K_2S_2O_3 + 48O_2 + H_2O = K_2S_2O_6 + H_2S_3O_6
\]

W. Spring (201) found that sulfur monochloride or
dichloride reacts with thiosulfate forming tetrathionate.

J. L. Gay Lussac (202) showed that thiosulfates are oxidized to sulfuric acid by nitric acid or aqua regia.

R. F. Weinland and A. Gutman (203) found that hyposo- sulfites do not reduce sodium thiosulfates.

6. Sulfoxylic Acid

When ethyl sulfide, \((\text{C}_2\text{H}_5)_2\text{S}\), is treated with nitric acid, it is oxidized to ethyl sulfoxide, \((\text{C}_2\text{H}_5)_2\text{SO}\), and to ethyl sulfone, \((\text{C}_2\text{H}_5)_2\text{SO}_2\).

E. Fromm and J. de Seixas Palma (204) attempted to prepare the so-called sulfur hydrate, or hydrogen sulfoxide, \(\text{S.H}_2\text{O}\), the hypothetical parent of the organic sulfoxides. Their attempts were unsuccessful. Also, H. Staudinger and W. Kreis (205) tried unsuccessfully to prepare sulfur monoxide, \(\text{SO}\).

I. Vogel and J. R. Partington (206) obtained sodium ethyl sulfoxylate, \(\text{Na}(\text{C}_2\text{H}_5)_2\text{SO}_2\), by the action of sodium ethoxide on sulfur sesquioxide; and when this is hydrolyzed, by allowing it to stand in contact with its mother-liquor overnight, sodium sulfoxylate, \(\text{Na}_2\text{SO}_2\), is formed. This salt is moderately soluble in cold and more soluble in hot water and sparingly soluble in alcohol. It is practically unattacked by boiling concentrated hydrochloric or sulfuric acids, but is attacked by a hot mixture of fuming nitric acid and bromine. The filtrate from the sodium sulfoxylate has a very unpleasant odor, and contains
salts of trithionic, sulfoxylic and sulfuric acids, and also small quantities of pentathionic and possibly tetra-thionic acids. The product of the reaction between sulfur sesquioxide and sodium ethoxide has a strongly alkaline reaction, and under these conditions any tetrathionate and pentathionate which might be produced would probably decompose with the formation of sulfites and thiosulfates, but the absence of the latter indicates that very little, if any, of these substances are produced in the initial reaction.

H. Bassett and R. G. Durrant (207) said that the resistance of sodium sulfoxylate to attack by boiling concentrated hydrochloric or sulfuric acid is highly improbable, and that the alleged sulfoxylate is more or less impure sodium sulfate, which is precipitated on adding sulfuric acid to a solution of a sodium compound in absolute alcohol.

Sulfoxylic acid, H_2SO_3, considered as the parent substance of organic sulfoxylates and sulfinates, is entirely a hypothetical compound which has never been isolated. Any postulates, therefore, as to its reactions and occurrence are lacking in experimental proof, and can be arrived at only by analogy and a consideration of the laws of kinetics.

Bassett and Durrant consider the reaction:

$$38(OH)_2 \rightleftharpoons H_2S + 2H_2SO_3$$

as improbable because it would be termolecular; and it is more likely that dissimilar molecules are respectively oxidized and reduced. They suggest that in alkaline solution, sulfoxylic acid forms the so-called anhydro-acid, disul-
foxylic acid, \( \text{H}_2\text{S}_2\text{O}_5 \text{OH} \), or pyrosulfoxylic acid:

\[
\text{S}2\text{(OH)}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}_2\text{S}_2\text{O}_5 \text{OH}
\]

Since many weak acids form pyro-salts in alkaline solution, e.g. boric acid, it is suggested that the sulfoxylic acid is reduced, and the disulfoxylic acid oxidized to pyrosulfurous acid, \( \text{H}_2\text{S}_2\text{O}_5 \), thus:

\[
\text{S(OH)}_2 + \text{H}_2\text{S}_2\text{O}_5 \text{OH} \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{S}_2\text{O}_5
\]

Disulfoxylic acid is isomeric with thiosulfuric acid.

The behavior of formaldehydesulfoxylates with metal salts, shows that in some cases, e.g. with arsenic trichloride, an increase in acidity favors the precipitation of arsenic sulfide instead of arsenic when free acid is present. In other cases, e.g. with sodium plumbite, an increase in alkalinity favors the formation of lead sulfide, while lead is precipitated as the alkalinity decreases. The reaction:

\[
\text{S(OH)}_2 + \text{H}_2\text{S}_2\text{O}_5 \text{OH} \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{S}_2\text{O}_5
\]

would proceed from left to right with a considerable increase in hydrogen ions, for there can be little doubt that sulfoxylic acid would be a very weak acid just as hypochlorous acid is. Alkali should, therefore, favor the change into sulfide and sulfite, which agrees with the results of the plumbite experiments. In acid solution high acidity might be expected to favor formation of anhydrosulfoxylic acid at the expense of sulfoxylic acid, and this also would accelerate the change of the latter into hydrogen sulfide and pyrosulfite. The effect of high acidity
in favoring precipitation of arsenious sulfide, rather than free arsenic, would then be intelligible. Increase in acidity would also tend to produce sulfur dioxide at the expense of either sulfurous or pyrosulfurous acid, and this also would hasten the decomposition of sulfoxylic acid. The reaction:

$$3(\text{OH})_3 + \text{H}_2\text{S} \rightleftharpoons 2\text{S} + 2\text{H}_2\text{O}$$

occurs with decrease of hydrogen ions, and will be favored by acidic conditions. It is this interaction of hydrogen sulfide and sulfoxylic acid which leads to the decomposition of sulfoxylic acid in acid solution in the absence of metals which form insoluble sulfides. Such decomposition could be represented by the summation equation:

$$2\text{S(OH)}_3 \rightleftharpoons \text{H}_2\text{SO}_3 + \text{S} + \text{H}_2\text{O}$$

When sulfoxylic acid is liberated by hydrolysis from its association with formaldehyde, it decomposes into sulfurous acid and hydrogen sulfide. If the hydrolysis occurs in the presence of lead, arsenic, antimony, stannous, bismuth, cadmium, nickel, cobalt, or zinc salts, the sulfide 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 sulfide fails to appear; 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 the absence of much acid, while, conversely, a little sulfide may be formed in the case of copper and silver in the presence of much acid. Precisely what happens in such cases depends upon the relative rates of the oxidation of sulfoxylic acid to sulfurous acid or of its change into hydrogen sulfide and sulfurous acid. These rates are effected by the concentration of reactants, acidity, and temperature. In the absence of salts of heavy metals, the hydrogen sulfide 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 sulfide and sulfurous acid leads to the formation of sulfur and polythionic acids. The acid hydrolysis of the formaldehydesulfoxylate occurs rapidly on heating, but is slow at ordinary temperatures; the actual rate depends also upon the acidity. The alkaline hydrolysis is extremely slow, but seems to follow a course similar to that of the acid hydrolysis, yielding sulfide and sulfite. The action of formaldehydesulfoxylate on sodium plumbite solutions is slow at ordinary temperatures but more rapid on heating. A mixture of metallic lead and lead sulfide is usually formed, a high concentration of sulfoxylate and high alkalinity being most favorable to the precipitation of lead sulfide. The reaction to metallic lead is due to the sulfoxylate, and not to the formaldehyde. In the presence of plumbite, it is the formation of insol-
uble lead sulfide which accelerates the hydrolysis of the formaldehydesulfoxylate. Sulfur will produce a similar effect by converting the sulfite, formed on hydrolysis of sulfoxylate, into thiosulfate. Thus, it was found that, after an alkaline solution of formaldehydesulfoxylate had been boiled with sulfur and the polysulfide (much of which was, of course, due to alkaline hydrolysis of the sulfur) removed with lead acetate, the solution was no longer capable of bleaching methylene blue. A similar alkaline sulfoxylate solution, after being boiled for the same length of time without sulfur, gave no precipitate with lead acetate and still had a strong bleaching action on methylene blue. On boiling an alkaline solution of sodium hydrosulfite to which sodium plumbite has been added, a greyish black precipitate of lead sulfide and metallic lead is obtained. The reaction occurs at ordinary temperatures but much more slowly. If the alkaline hydrosulfite 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 sulfide, if only small quantities of hydrosulfite and plumbite are used in the experiment. Bassett and Durrant could find no positive evidence in support of the assumption that sulfoxylic acid decomposes:

\[
28(\text{OH})_2 = \text{H}_2\text{S} + \text{H}_2\text{SO}_4 \quad \text{and} \\
28(\text{OH})_2 = \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}
\]
They added that if sulfoxyllic acid could undergo either of these changes, alkalies should promote the changes, since both would correspond to a considerable increase in hydrogen ion. No sulfate is produced when sodium formaldehydesulfoxylate is boiled with a solution of sodium plumbite; nor is any produced when sodium formaldehydesulfoxylate is hydrolysed in acid solution either alone or in the presence of lead or arsenious salts. If the arsenious sulfide formed had resulted from the decomposition of the thiosulfate, large amounts of sulfate would have been produced. No change was observed when an alkaline solution of sodium formaldehydesulfoxylate was heated for a long time.

If a concentrated solution of hyposulfite is added to a concentrated solution of hydrochloric acid, sulfur separates at once; but with a concentrated solution of thiosulfate, sulfur does not separate for a long time. If the sulfoxyllic acid formed on hydrolysis of the hyposulfite changed rapidly into thiosulfate, no separation of sulfur is likely to have occurred. The observed separation of sulfur is not due to the presence of sulfite, for a solution of an equal molar mixture of sodium pyrosulfite and thiosulfate did not yield any sulfur when added to concentrated hydrochloric acid, except after long standing.

7. Hyposulfurous Acid

In 1718, G. E. Stahl (208) observed that iron dis-
solves in sulfurous acid forming a reddish yellow liquid; and C. L. Berthellet (209) observed that no gas is given off in the reaction. A. F. de Fourcroy and L. N. Vauquelin (210) showed that a similar reaction occurred with tin and zinc.

C. F. Sehobein (211) and others noticed that the electrolysis of sulfurous acid yielded a liquid similar to the one discussed in the proceeding paragraph and that they were further similar in that both are strong reducing agents and contain an acid with less oxygen than that contained in sulfurous or rather thiosulfuric acid.

E. Mitscherlich (212) thought that the acid thus formed was thiosulfuric acid while H. Risler-Beunat (213) said that pentathionic acid was formed.

M. J. Fordos and A. Gelis (214), C. Geitner (215), and A. Harpf (216) reported sulfuric, thiosulfuric, tri-thionic, and pentathionic acids, as well as hydrogen sulfide as products.

P. Schützenberger (217) recognized the acid as a new acid and called it l'acide hydrosulfureus, that is hydrosulfurous acid. He also prepared a number of salts of the acid.

H. E. Roscoe and C. Schorlemmer (218) and R. von Wagner (219) preferred the name hyposulfurous acid and they called the salts hyposulfites.

Further work established the formula of hyposulfurous acid as $\text{H}_2\text{S}_2\text{O}_4$. 
As indicated above, hyposulfurous acid is prepared by dissolving iron or zinc in sulfurous acid contained in a closed vessel. According to P. Schutzenberger (217) the reaction may be represented by the following equation:

\[ 2\text{H}_2\text{S}_2\text{O}_3 + 2\text{H}_2 = (\text{H}_2\text{SO}_4)\_2 + 2\text{H}_2\text{O} \]

W. Spring (220) showed that the acid is formed along with tetrathionic acid when hydrogen sulfide is passed into sulfurous acid; L. Maquenne (221) when sulfurous acid is reduced by hypophosphorus acid; S. Kapff (222) by formic acid or sodium formate; and A. Guerout (223) by the electrolysis of sulfurous acid. Sulfuric acid is formed at the anode and hyposulfurous acid is formed at the cathode with a low current density and sulfur with a high current density. C. Luckow (224) also noted the formation of sulfur and hydrogen sulfide.

The aqueous solution of the free acid is stable for only a short time. P. Schutzenberger (225) obtained it by decomposing the sodium salt with dilute sulfuric or oxalic acid; and R. Englert and F. Becker (226) by treating a solution of the calcium salt with sulfuric, oxalic, or phosphoric acid.

P. Schutzenberger (225) made the sodium salt by the action of zinc on a solution of sodium hydrosulfite in a well cooled vessel:

\[ 6\text{NaHSO}_3 + 2\text{Zn} = 2\text{ZnSO}_3 + 2\text{H}_2\text{O} + 2\text{Na}_2\text{SO}_3 + (\text{NaHSO}_3)\_2 \]

A. Bernthsen (227) measured the rate of conversion of the sulfur of hydrosulfate into hyposulfite with solu-
tions containing different proportions of salt in solution.

J. Volhard (228) obtained the hyposulfite as an intermediate stage in the action of sulfur dioxide on an alkali sulfide.

According to E. H. Eckler (229), sodium hyposulfite is oxidized to sulfate electrolytically at the anode; and K. Elbs and K. Becker (230) said that at the cathode the hyposulfite is reduced to thiosulfate:

$$Na_2S_2O_4 + 2H = H_2O + Na_2S_3O_3$$

K. Jellinek (231) showed that sodium hyposulfite, in solutions containing hydrogen sulfite, decomposes spontaneously into thiosulfate and hyposulfite, and then hydrosulfite:

$$2Na_2S_2O_4 = Na_2S_3O_3 + Na_2S_3O_5$$

$$Na_2S_3O_5 + H_2O = 2NaHSO_3$$

In concentrated solutions the rate of decomposition is practically unaffected by the presence of platinum or lead, while in dilute solutions the greater part of the change takes place at the surface of the platinized platinum plate. He showed that the stationary condition, in which the concentration of hyposulfite does not increase, is reached when the rate of formation of hyposulfite by the current is equal to its rate of spontaneous decomposition, from which it follows that the hyposulfite is not reduced electrolytically, and that in order to obtain a high concentration in solution it is only necessary to increase the rate of formation by applying a large current
to a small volume of solution.

Hyposulfurous acid is known only in dilute aqueous solution. P. Schutzenberger (232) and A. Bins (233) found that an aqueous solution of the hyposulfites decompose when warmed forming only hydrosulfites; but J. Meyer (234) represented the reaction:

$$2\text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} = \text{Na}_2\text{S}_3\text{O}_3 + 2\text{NaHSO}_3$$

The speed of the decomposition is slow at the start then rises to a maximum and again slows down. Part of the products of the decomposition react with the undecomposed salt and consequently the velocity of decomposition is proportional both to the extent of the decomposition and to the quantity of salt left undecomposed. E. Jellinek (235) found $k$ at $20^\circ$ to be 0.00037.

K. Jellinek (236) studied the decomposition of sodium hyposulfite in solutions of sodium sulfite or hydrosulfite and found that it can be represented as a unimolecular reaction.

C. K. Jableczynsky and Z. Warszawska-Rytel (237) found that the rate of decomposition is accelerated by the addition of sodium chloride, and diminished by the addition by the addition of a colloid like gum arabie. Dilution retards decomposition. The speed of the reaction corresponds to two reactions of the first order. C. F. Schonbein (238), P. Schutzenberger (232), and A. R. Frank (239) showed that the decomposition is retarded in the presence of alkalies.
Acidic solutions decompose very quickly, for when a solution of the sodium salt is acidified, it becomes yellow or orange and much sulfur is separated.

When hyposulfurous acid is liberated from its salts, it is readily hydrolysed to sulfoxylic and sulfurous acids. H. Bassett and R. G. Durrant (240) summarize the reaction:

\[ \text{HO}_2\text{S}_2\text{O}_3\text{OH} \rightleftharpoons (\text{HO})_2\text{S}_2\text{O}_4 \]  
\[ \text{HO}_2\text{S}_2\text{O}_3\text{OH} + \text{H}_2\text{O} = \text{S(OH)}_2 + \text{H}_2\text{SO}_3 \quad (\rightleftharpoons \text{H}_2\text{O} + \text{SO}_3) \]

and

\[ \text{S(OH)}_2 + \text{SO}_3 \rightleftharpoons (\text{HO})_2\text{S}_2\text{O}_4 \]

Thus two isomeric forms of \( \text{H}_2\text{S}_2\text{O}_4 \) are assumed. The direct union of two sulfur atoms in \( (\text{HO})_2\text{S}_2\text{O}_4 \) indicates that the compound can probably be readily reduced to thiosulfate; and this is in agreement with K. and E. Jellinek's (241) observation that hyposulfurous and thiosulfuric acids are successive stages in the electrolytic reduction of sulfurous acid. The oxidation of \( \text{HO}_2\text{S}_2\text{O}_3\text{OH} \) by \( (\text{HO})_2\text{S}_2\text{O}_4 \) is taken to explain the change of the hyposulfite into thiosulfate and pyrosulfite:

\[ \text{HO}_2\text{S}_2\text{O}_3\text{OH} + (\text{HO})_2\text{S}_2\text{O}_4 \rightleftharpoons \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{S}_2\text{O}_6 \]

The reaction was found to be bimolecular.

In the presence of acids, there is superposed on these changes the reactions:

\[ \text{H}_2\text{S} + \text{S(OH)}_2 \rightleftharpoons 2\text{S} + 2\text{H}_2\text{O} \]

\[ \text{S(OH)}_2 + \text{HO}_2\text{S}_2\text{O}_3\text{OH} \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{S}_2\text{O}_6 \]

There is also the possible formation of polythionates by the interaction of hydrogen sulfide and sulfurous
acid, or by the decomposition of thiosulfate.

The dominant quality of hyposulfurous acid, or rather of the hyposulfites, is a strong reducing action. The hyposulfites are readily oxidized. A. and L. Lumiere and A. Seyewetz (243) found that when a thin layer of powdered anhydrous sodium hyposulfite is exposed to the action of moist air, it is completely decomposed in seven days, but is practically stable in a closed vessel or in dry air, the slow changes observed, ten and four percent loss of sodium hyposulfite, respectively, in two months being due to the addition of moisture in removing the daily samples. Solutions of sodium hyposulfite in boiled distilled water in closed vessels decompose at rates varying with the concentration; 25, 10, and 3 percent solutions are decomposed in 3, 11, and 37 days, respectively. The rate of change is accelerated by a rise of temperature or by an exposure of the solution to the air; in the latter case, the relative stabilities are reversed, a 3 percent solution decomposing in one, a 20 percent solution in two days. The decomposition takes place as follows:

\[ 2Na_2S_2O_4 = 2Na_2S_2O_3 + Na_2S_2O_6 \]

\[ Na_2S_2O_4 + O = Na_2SO_3 + SO_3 \]

sodium hyposulfite being formed in aqueous solution. The chief product of the reaction is the sulfite.

When shaken with air or oxygen, P. Schutzenberger (243) and co-workers found that solutions of the hyposulfite become yellow or orange, and finally colorless.
The yellow coloration is due to the liberation of free acid. Twice as much oxygen is absorbed as is needed to convert the hyposulfite into hydrosulfite, but J. Meyer (244) found that the quantity absorbed is not quite twice that needed to form the sulfite; and he said that the excess of oxygen is used in carrying the oxidation past the sulfite stage:

$$H_2S_2O_4 + O_2 + H_2O = H_2SO_4 + H_2SO_3$$

and to a small extent

$$2H_2S_2O_4 + O_2 + 2H_2O = 4H_2SO_3$$

Mild oxidizing agents, e.g. silver salts, normally oxidize hyposulfite to sulfite, but with molecular oxygen, J. Meyer (244) said that during the oxidation of the hyposulfites, sulfite and sulfate, as well as thiosulfate, and dithionate may be formed; and the sulfate and sulfite would be in equal molar proportions were it not for disturbances produced by the hydrolysis of the hyposulfite by the acid formed during the oxidation. H. Bassett and R. G. Durrant (245) added that with solutions containing sufficient sodium carbonate to neutralize the acid formed, the atmospheric oxidation of hyposulfite proceeds smoothly as a unimolecular reaction.

J. Meyer (244) found that hydrogen dioxide oxidizes hyposulfites in acidic or alkaline solutions, forming sulfates, and a small proportion of dithionates.

The hyposulfites were found by A. Bernthsen (248) to be oxidized by iodine to sulfates.
Brotherton and Company (247) represented the reaction with sodium hyposulfite and potassium iodate:

$$3Na_2S_2O_3 + 4KIO_3 + 2KI = 3I_2 + 3Na_2SO_4 + 2K_2S_2O_4$$

W. Spring (248) found sulfur to be without action on sodium hyposulfite; and L. Tschugaeff and W. Chlopin (249) observed that a warm solution of sodium hydromide and hyposulfite attacks sulfur to a very slight extent.

A. Bins (250) showed that while the hyposulfite has no action on sodium sulfide, it reacts vigorously with sodium polysulfides:

$$Na_2S_2O_3 + Na_2S_n + H_2O = NaS.30.0H + NaS.30.0H + Na_2S_n-2$$

but these products immediately decompose giving off hydrogen sulfide; with sodium polysulfide and hydroxide:

$$Na_2S_2O_3 + Na_2S_x + 4NaOH = 2Na_2SO_3 + 2Na_2S + 2H_2O$$

$$2Na_2S_2O_3 + 2Na_2S_x + 2NaOH = 2Na_2S + 3Na_2S_2O_3 + H_2O$$

and with an excess of polysulfide:

$$Na_2S_2O_3 + Na_2S_n + 4NaOH = 2Na_2S_2O_3 + Na_2S + Na_2S_n-2$$

$$+ 2H_2O$$

A. Bins and W. Sondag (251) found that the reaction in alkaline solution can be represented:

$$Na_2S_2O_3 + Na_2S_2O_3 + 4NaOH = 3Na_2SO_3 + Na_2S + 2H_2O$$

W. Spring (248) showed that if hydrogen sulfide be passed into a feebly acidified solution of potassium hyposulfite, the liquid becomes hot, sulfur is precipitated and the liquid no longer decolorizes indigo; if the solution be neutralized with potassium carbonate, the sulfur is deposited, and potassium thiosulfate, precipitable with alcohol, is formed.
The Polythionic Acids

The polythionic acids have the general formula $H_nS_nO_6$ where $n$ ranges from 2 to 6.

Dithionic Acid $H_2S_2O_6$

Trithionic Acid $H_3S_3O_6$

Tetrathionic Acid $H_4S_4O_6$

Pentathionic Acid $H_5S_5O_6$

They are formed when sulfur dioxide, water, and sulfur in status nascendi react with one another under different conditions.

J. Dalton (252) observed that sulfur dioxide and hydrogen sulfide react in aqueous solution producing an acid. T. Thomson (253) considered this acid as a sulfo-sulfurous acid. H. W. F. Wackenroder (254) suspected the presence of pentathionic acid in the products of the reaction, and the solution was afterwards called Wackenroder's liquid.

A. Sobrero and F. Sälmi (256), and T. Curtius and F. Henkel (257) observed that besides pentathionic acid there occurs in the solution tetrathionic, thiosulfuric, and sulfuric acids, but M. J. Fordos and A. Gelis (258) said that these latter products were decomposition products of the initial pentathionic acid.

H. Debus (259) after a thorough study of Wackenroder's solution gave the following as being in the solution:

(1) Small drops of sulfur in suspension

(2) Sulfur in the colloidal state
(3) Sulfuric acid
(4) Traces of trithionic acid
(5) Tetrathionic acid
(6) Pentathionic acid
(7) Hexathionic acid (?)

Debus showed that hydrogen sulfide and sulfur dioxide in water react with the separation of sulfur. Pentathionic acid is not the direct product of the reaction because the greater part of the polythionic acid appears only after the solution has been allowed to stand for four or five hours. The quantity of tetrathionic acid formed is independent of the time of preparation, and it is, therefore, inferred that tetrathionic acid is the primary product of the reaction:

$$3\text{SO}_2 + \text{H}_2\text{S} = \text{H}_2\text{S}_4\text{O}_6$$

Since both sulfur dioxide and hydrogen sulfide act on tetrathionic acid the final mixture is rather complex as shown above.

As long as the sulfur dioxide is in excess as is the case in the beginning of the reaction (hydrogen sulfide passed into sulfurous acid), most of the hydrogen sulfide reacts with the sulfurous acid, forming tetrathionic acid and we only have to consider the secondary reaction of the sulfurous acid on the tetrathionic acid. This reaction has been found to yield trithionic and thiosulfuric acids in a reversible equation. The thiosulfuric acid can then react with the tetrathionate to give pentathionic
acid, so that the solution now contains sulfurous, thio-
sulfurous, tri-, tetra-, and pentathionic acids.

Now, if hydrogen sulfide be passed in in excess,
the hydrogen sulfide attacks the tetrathionic acid forming
water and sulfur. This sulfur *in statu nascendi* converts
trithionic into tetrathionic acid; tetrathionic into penta-
thionic acid; and pentathionic into hexathionic acid.
The moment all of the sulfurous acid disappears the tri-
thionic acid is converted into tetrathionic acid. Some
of the sulfur produced remains in solution as colloidal
sulfur and part separates as a suspension. If hydrogen
sulfide is passed through the solution for some time it is
found that the final products are sulfur and water:

\[ 2H_2S + SO_2 = 3S + 2H_2O \]

all other products being intermediate products. Any sul-
furic acid appearing in the reaction is thought to be due
to atmospheric oxidation of sulfurous acid.

H. Bassett and R. G. Durrant (260) represent the
reaction in a somewhat different manner. They claim that
the first stage of the reaction between sulfurous acid
and hydrogen sulfide is:

\[ H_2S + H_2S_2O_8 \rightleftharpoons H_2S_3O_8 + S(OH)_2 \]

Hence, sulfoxyclic and its pyro derivative represent the
first product of the reaction. The sulfoxyclic acid reacts
with the hydrogen sulfide to form sulfur:

\[ S(OH)_2 + H_2S \rightleftharpoons 2H_2O + 2S \]

and the freshly formed sulfur is in a favorable condition
for reaction with sulfurous acid to form thiosulfuric acid:

\[ S + H_2SO_3 \rightleftharpoons H_2S_2O_3 \]

which is relatively stable in weak acidic solution. Thri-thionic acid is formed from the thiosulfuric acid:

\[ 2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_2O_6 \]

and some trithionate may be formed from sulfurous and sulfoxylic acid:

\[ 2S(OH)_2 + H_2SO_3 = H_2O + HO.SO_4.S.OH \]

F. Forster and R. Vogel (861) suggested the reaction:

\[ SO + 2HSO_3^- = S_2O_8^{2-} + H_2O \]

for the trithionate formation.

Bassett and Durrant found that traces of polythionates are formed by shaking sulfurous acid with a solution of sulfur in benzene; and by passing sulfur dioxide and sulfur vapor simultaneously into an aqueous solution of sulfurous acid, a mixture of thithionic and tetrathionic acids was obtained.

F. Forster and K. Centner (262) also concluded that some trithionate is formed directly:

\[ S_2O_8^{2-} + 4HSO_3^- + 2H^+ = 2S_2O_6^{2-} + 3H_2O \]

and not by the degradation of pentathionic acid.

The hypothesis of Bassett and Durrant can be adapted to explain the results of H. Debus (263), and of E. H. Riesenfeld and G. W. Feld (264) as well as the hypothesis based on the primary formation of sulfoxylic acid:

\[ H_2SO_3 + H_2S \rightleftharpoons H_2SO_4 + H_2SO \]

or, the hypothesis of E. H. Riesenfeld and G. W. Feld.
based on the primary reaction:

\[ \text{H}_2\text{S} + 2\text{H}_2\text{SO}_3 = 3(\text{HO})_2\text{S} \text{ (or SO + H}_2\text{O)} \]

or the hypothesis of F. Forster and A. Hornig (265)

based on the primary reaction:

\[ \text{H}_2\text{S} + 2\text{H}_2\text{SO}_3 = \text{H}_2\text{S}_2\text{O}_2 + \text{H}_2\text{O} \]

No proof of the primary formation of sulfoxylic acid is possible except that it bleaches indigo, but this test is ambiguous since hyposulfurous acid gives a similar action.

F. Raschig (266), E. H. Riesenfeld and G. W. Feld (264), F. Forster (267), and A. Kurtenacker and M. Kaufmann (268) have suggested hypotheses in which pentathionic acid is the first formed polythionic acid, while Bassett and Durrant claim trithionic is first and pentathionic is the last polythionic acid formed. They claim that the higher polythionic acids are built up from trithionic acid by the assimilation of sulfur:

\[ \text{H}_2\text{S}_2\text{O}_4 + \text{S} = \text{H}_2\text{S}_4\text{O}_6 \]
\[ \text{H}_2\text{S}_4\text{O}_6 + \text{S} = \text{H}_2\text{S}_6\text{O}_8 \]

The order of the stability of trithionic, tetrathionic, and pentathionic acids is as follows: Tetrathionic acid is the least stable and readily decomposes into tri- and pentathionic acids. Trithionic acid decomposes more slowly into sulfur dioxide. Pentathionic acid decomposes only in the course of months with the separation of sulfur.

In alkaline solution all of the polythionates decompose quickly into thiosulfate and sulfite.
The phenomena observed are explained on the assumption that the intermediate compound is the hydrate of the unknown sulfur monoxide, $\text{SO}_2$. This is stable in acid solution for a time but in neutral or alkaline solution quickly forms thiosulfate. In acid solution it slowly polymerizes to pentathionic acid. By combination with sulfurous acid it forms tri- and tetrathionic acids:

$$3\text{SO}_2 + \text{H}_2\text{SO}_4 = \text{H}_2\text{S}_4\text{O}_6$$

$$\text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{S}_2\text{O}_6$$

with hydrogen sulfide it is reduced to sulfur.

F. Forster (269) assumed that in aqueous solution there is a state of equilibrium between sulfoxylic acid and its hypothetical anhydride:

$$\text{H}_2\text{SO}_2 \rightleftharpoons \text{SO}_2 + \text{H}_2\text{O}$$

and that the other sulfur acids are formed by the reactions:

1. $\text{SO}_2 + \text{H}_2\text{S} = 2\text{S} + \text{H}_2\text{O}$

2. $2\text{SO}_2 + \text{H}_2\text{O} = \text{S}_2\text{O}_3^- + 2\text{H}^+$

3. $\text{SO}_2 + 2\text{H}_2\text{SO}_3^- = \text{S}_2\text{O}_6^{2-} + \text{H}_2\text{O}$

4. $\text{SO}_2 + 2\text{H}_2\text{SO}_3^- = \text{S}_2\text{O}_6^{2-} + \text{H}_2\text{O}$

He also assumed that the initial reactions in the formation of Wackenroder's solution involve:

$$\text{H}_2\text{S} + \text{H}_2\text{SO}_3 = \text{S}_2(\text{OH})_2 + \text{H}_2\text{O}$$

followed by:

$$\text{S}_2(\text{OH})_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2\text{SO}_4$$

and

$$\text{S}_2(\text{OH})_2 + \text{H}_2\text{S} \rightleftharpoons 2\text{H}_2\text{O} + 2\text{S}$$

Equation 3 is preferred to that suggested by H. Bassett and R. G. Durrant (270) for the formation of trithionic acid.
F. Forster and A. Hornig (265) represented the reaction between sulfurous acid and hydrogen sulfide as a balanced process involving the intermediate formation of the hypothetical \(\text{H}_2\text{S}_2\text{O}_3\):

\[
\text{H}_2\text{S} + \text{H}_2\text{SO}_3 \rightleftharpoons \text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}
\]

but a further reaction with hydrogen sulfide produces sulfur, while an excess of sulfurous acid produces pentathionic acid. They added that the trithionates are the least stable, and the tetrathionates the most stable.

None of the polythionic acids are stable in aqueous solution, and the following decompositions occur in solution:

\[
\begin{align*}
\text{S}_2\text{O}_4^{-} & \rightleftharpoons \text{S}_4\text{O}_6^{-} + \text{S} \\
\text{S}_4\text{O}_6^{-} & \rightleftharpoons \text{S}_2\text{O}_3^{-} + \text{S} \\
\text{S}_2\text{O}_3^{-} + \text{H}_2\text{O} & = \text{SO}_4^{2-} + \text{S}_2\text{O}_3^{-} + 2\text{H}^+ \\
\text{S}_2\text{O}_3^{-} + \text{H}^+ & \rightleftharpoons \text{HSO}_3^{-} + \text{S}
\end{align*}
\]

The insolubility of sulfur removes it from equilibrium, and at boiling temperatures the sulfur dioxide is removed and sulfate is left alone in solution; side reactions were also shown to take place. The more sulfur dioxide and sulfur there remains in solution, the greater is the tendency of thiosulfuric acid to polymerize, e.g.

\[
\begin{align*}
\text{S}_2\text{O}_3^{-} + \text{S}_2\text{O}_3^{-} + \text{H}^+ & \rightleftharpoons \text{S}_4\text{O}_6^{-} + \text{HSO}_3^{-} \\
\text{S}_4\text{O}_6^{-} + \text{S}_2\text{O}_3^{-} + \text{H}^+ & \rightleftharpoons \text{S}_6\text{O}_8^{-} + \text{HSO}_3^{-}
\end{align*}
\]

A high concentration of hydrogen ions retards the decomposition of tetra- and pentathionic acids, but not of trithionic acid. F. Forster (272) also said that in addition to the formation of thiosulfate:
The intermediate product, sulfur monoxide, may produce polythionic acids by other changes, e.g.

\[
2\text{SO} + 2\text{H}_2\text{O} \rightleftharpoons \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ 
\]

Dithionic Acid

Dithionic acid, \( \text{H}_2\text{S}_2\text{O}_6 \), may be prepared by passing sulfur dioxide into water with manganese dioxide in suspension. Upon the addition of barium hydroxide solution, the sulfate is precipitated out leaving barium dithionate in solution. This method was developed by J. L. Gay Lussac and J. J. Welter (275).

The aqueous solution of the acid is without odor and upon concentrating past sp. gr. 1.347 decomposes into sulfur dioxide and sulfuric acid.

In general dithionic acid arises from the oxidation of sulfurous acid with very mild oxidants such as manganese dioxide or the hydroxides of the tervalent iron family.

The reaction with ferric hydroxide is:

\[
2\text{Fe(OH)}_3 + 3\text{SO}_2 = \text{FeS}_2\text{O}_6 + \text{FeSO}_3 + 3\text{H}_2\text{O} 
\]

F. Heeren (274) and T. S. Dymond and F. Hughes (275) found that an acidic solution of potassium permanganate oxidizes sulfurous acid to the dithionate. H. Buignet (276) said that the permanganate is first reduced to \( \text{MnO}_2 \) which then acts as indicated above:

\[
2\text{KMnO}_4 + 3\text{SO}_2 + 2\text{H}_2\text{O} = 2\text{KHSO}_4 + 2\text{MnSO}_4 + \text{H}_2\text{S}_2\text{O}_6 
\]
A. Friessner (277) and co-workers studied the electro-oxidation of neutral and alkaline solutions of sodium sulfite with high anodic potentials and obtained dithionate under the proper conditions according to the equation:

$$2\text{SO}_3^- + 2\text{OH}^- + 2\text{H}^+ + 2(\equiv) = \text{S}_2\text{O}_3^{2-} + 2\text{H}_2\text{O}$$

A. Nabl (278) observed that when a 33% solution of sodium thiosulfate is mixed with the calculated quantity of hydrogen peroxide, and acid added from time to time to keep the liquid neutral, sodium dithionate is formed:

$$2\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}_2 = 2\text{NaOH} + \text{Na}_2\text{S}_2\text{O}_3$$

If an excess of hydrogen peroxide is used the dithionate is oxidized to sulfate:

$$\text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{SO}_4$$

L. P. de St. Filles (279) observed that an acidic solution of potassium permanganate oxidizes thiosulfate to dithionate.

M. J. Fordos and A. Gelis (280) found that trithionates yield dithionate when treated with acid potassium permanganate solution.

J. Meyer (281) observed that acidic and alkaline solutions of hyposulfurous acid are oxidized by hydrogen peroxide to sulfuric and dithionic acids.

Dithionic acid has never been isolated but exists only in aqueous solution. The alkaline and alkaline earth salts are stable both in solution and in the solid state at temperatures below 100°.

Oxidizing agents can transform dithionic acid into
sulfuric acid but as stated by A. Fischer and W. Classen (282) sodium dithionate is not readily attacked by cold alkaline or neutral oxidants, and but little in acidic solution.

A. Longi and L. Bonavia (283) found that sodium dioxide oxidises the dithionates to sulfates slowly.

J. L. Gay Lussac and J. J. Welter (284) said that the cold aqueous solution of the acid is not oxidized by a cold aqueous solution of chlorine, but is oxidized in a boiling solution; and A. J. Balard (285) found that the cold solution is not oxidized by hypochlorous acid.

F. Heeren (286) found that dithionic acid had no effect on hydrogen sulfide and H. C. H. Carpenter (287) found no action for sulfur dioxide on barium dithionate.

Dithionates are not decomposed by boiling with alkali.

9. Trithionic Acid

Potassium trithionate was first prepared by C. Langlois (288) in 1840 by the action of sulfur on potassium hydrosulfite:

\[ 6KHSO_3 + 2S = 2K_2S_2O_3 + K_2S_2O_5 + 3H_2O \]

Trithionic acid has never been isolated. The acid slowly decomposes at ordinary temperatures with the separation of sulfur, the evolution of sulfur dioxide, and the formation of sulfuric acid:

\[ H_2S_3O_6 = H_2SO_4 + SO_2 + S \]

M. J. Fordos and A. Gelis (289) said that the solution
of the acid is more stable in the presence of acid.

The sulfur does not all separate in the free state during the decomposition, but part of it reacts with trithioninic acid to form pentathioninic acid and probably tetrathioninic acid. The test for pentathioninic acid is positive after standing 14 days.

$$3\text{H}_2\text{S}_2\text{O}_6 = 2\text{H}_2\text{SO}_4 + 2\text{SO}_3 + \text{H}_2\text{S}_2\text{O}_6$$

Similarly, a clear neutral solution of potassium trithionate yields a test for tetrathioninic acid upon standing twenty-four hours.

$$2\text{K}_2\text{S}_2\text{O}_6 = \text{K}_2\text{S}_4\text{O}_6 + \text{K}_2\text{SO}_4 + \text{SO}_2$$

After six days a test for pentathioninate was obtained.

A. Kurtenacker and M. Kaufmann (290) represented the reactions as follows:

1. $$\text{S}_2\text{O}_6^{2-} + \text{H}_2\text{O} = \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + 2\text{H}^+$$
2. $$\text{S}_2\text{O}_3^{2-} + \text{S}_2\text{O}_6^{2-} + \text{H}^+ = \text{S}_4\text{O}_6^{2-} + \text{HSO}_3^-$$
3. $$5\text{S}_2\text{O}_6^{2-} + 6\text{H}^+ = 2\text{S}_4\text{O}_6^{2-} + 3\text{H}_2\text{O}$$
4. $$\text{S}_2\text{O}_3^{2-} + \text{H}^+ = \text{HSO}_3^- + \text{S}$$

C. Saintpierre (291) found that if a dilute solution of potassium hydrosulfite be heated in a sealed tube on a water bath, sulfur, and potassium trithionate and sulfate are formed but no other sulfur compound:

$$10\text{KHSO}_3 = 5\text{K}_2\text{SO}_4 + \text{H}_2\text{S}_2\text{O}_6 + 2\text{S} + 4\text{H}_2\text{O}$$

The liquid first become yellow presumably due to the formation of sulfur so that here again the trithionate is produced by the action of sulfur on the hydrosulfite.

Since sulfur dioxide acts on potassium thiosulfate to form
the trithionate, it follows that the action of sulfur on potassium hydrosulfite proceeds in two stages:

\[ 3K_2S_2O_8 + 3S = 2K_2S_3O_6 + 3SO_2 + K_2S_2O_6 \]

and

\[ K_2S_2O_8 + 3SO_2 = 2K_2S_3O_6 + S \]

G. Chancel and E. Diacon (292) produced trithionate by the action of sulfur dioxide on a mixed solution of potassium sulfide and hydrosulfite:

\[ K_2S + 4KHSO_3 + 4SO_2 = 3K_2S_2O_6 + 2H_2O \]

E. Mathieu-Plessy (293) observed that potassium trithionate is formed by the action of sulfur dioxide on a concentrated solution of potassium thiosulfate:

\[ 2K_2S_2O_8 + 3SO_2 = 2K_2S_3O_6 + S \]

A. Villiers (294) said that the reaction with sodium thiosulfate should be represented by:

\[ 2Na_2S_2O_3 + 3SO_2 = Na_3S_4O_6 + Na_2S_3O_6 \]

H. Debus (295) showed that Mathieu-Plessy's equation could not be right because the final products of the reaction are potassium trithionate as the main product, while sulfur and potassium tetra- and pentathionates are also formed:

\[ 6K_2S_2O_8 + 9SO_2 = K_2S_2O_6 + K_2S_4O_6 + 4K_2S_3O_6 \]

Actually less penta- and tetrathionate and more trithionate are formed due to the formation of sulfur.

B. Rathke (296) showed that the trithionate is produced if a mixture of potassium thiosulfate and hydrosulfite be crystallized together:

\[ 2K_2S_2O_8 + 3SO_2 = 2K_2S_3O_6 + S \]
The oxidation of a solution of sodium sulfite and thiosulfate by means of iodine yields trithionate according to W. Spring (297):

\[ \text{Na}_2\text{SO}_3 + \text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_3\text{O}_6 + 2\text{NaI} \]

but A. Colfax (298) said that his is not correct, for the trithionate is the result of a secondary reaction between tetrathionate and sulfite in the presence of iodine.

R. Willstätter (299) obtained the trithionate by dropping hydrogen dioxide into a solution of sodium thiosulfate at 0° to 10°:

\[ 2\text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O} = \text{Na}_2\text{S}_3\text{O}_6 + \text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O} \]

J. E. Mackenzie and H. Marshall (300) showed that while tetrathionates are produced by the action of persulfates on thiosulfates:

\[ \text{K}_2\text{S}_2\text{O}_3 + 2\text{Sr}_2\text{S}_2\text{O}_3 = 2\text{SrSO}_4 + \text{K}_2\text{S}_4\text{O}_6 \]

provided a slight excess of the persulfate is used; if the thiosulfate be in excess, the trithionate is produced.

P. Pierron (301) found that trithionate is formed in the anodic oxidation of a solution of ammonium thiosulfate. As indicated in connection with Wackenroder's liquid, trithionic acid is formed among the products of the decomposition of the polythionic acids; and also by the action of sulfur dioxide on these acids.

H. Honig and E. Zatzek (302) found that trithionate was produced along with sulfuric acid and sulfur by the action of potassium permanganate in the cold on alkali sulfides or polysulfides.
According to W. Spring (303) sulfur monochloride reacts with potassium sulfite forming trithionate:

\[ 2K_2SO_3 + S_2Cl_2 = K_2S_3O_6 + 2KCl + S \]

and with sulfur dichloride:

\[ 2K_2SO_3 + SCl_2 = K_2S_3O_6 + 2KCl \]

H. Debus (304) said that water decomposes sulfur monochloride into thiosulfuric and hydrochloric acids and sulfur:

\[ 2S_2Cl_2 + 3H_2O = H_2S_2O_3 + 4HCl + 2S \]

The thiosulfuric acid soon splits into water, sulfur, and sulfurous acid. Whenever nascent sulfur and sulfurous acid meet under favorable conditions, polythionic acids are formed, and he detected the presence of pentathionic acid in the liquid.

The hydrolysis of trithionic acid in acidic solution can be represented by:

\[ H_2S_3O_6 + H_2O \rightleftharpoons H_2S + H_2S_2O_7 \]

and

\[ 2H_2S_2O_3 + 3H_2O \rightleftharpoons 2H_2S + 2H_2SO_4 \]

According to F. Forster and A. Hornig (305) the hydrolysis in weakly acidic and weakly alkaline solutions can be represented by:

\[ H_2S_3O_6 + H_2O = H_SO_4 + H_2S_2O_3 \]

In the presence of sodium acetate the above reaction is quantitative.

The hydrolysis in strongly alkaline solution is:

\[ 2H_2S_2O_3 + 3H_2O \rightleftharpoons H_2S_2O_3 + 4H_2SO_3 \]

A. Sander (306) represented the reaction with hydrogen peroxides:
Na_{2}S_{3}O_{6} + 4H_{2}O + 4NaOH = 3Na_{2}SO_{4} + 6H_{2}O

A. Longi and L. Bonivia (307) found that sodium dioxide completely oxidizes thiosulfates to sulfates. According to M. Berthelot (308) when chlorine is passed into a solution of trithionate, sulfate is formed. The same action was observed with bromine.

C. Langlois (309) said that hydrochloric acid was without action on trithionates; chloric acid oxidizes trithionic acid to sulfur and sulfuric acid; perchloric acid is without action.

H. Debus (310) represented the reversible action of sulfur on trithionates as:

\[ K_{2}S_{3}O_{6} + S \rightleftharpoons K_{2}S_{4}O_{6} \]

and \[ K_{2}S_{3}O_{6} + 2S \rightleftharpoons K_{2}S_{5}O_{6} \]

Debus said hydrogen sulfide was without action on trithionates at ordinary temperature. On prolonged standing the following may take place:

\[ 2K_{2}S_{3}O_{6} + 5H_{2}S = K_{2}SO_{4} + K_{2}S_{2}O_{3} + 5H_{2}O + 8S \]

G. Chancel and E. Diacon (311) and A. Kurtenacker and W. Kaufmann (312) found that potassium sulfide converts the trithionate into thiosulfate without the separation of sulfur:

\[ K_{2}S_{3}O_{6} + K_{2}S = 2K_{2}S_{2}O_{3} \]

Debus showed that if a solution of trithionic acid be treated with sulfur dioxide, all three polythionic acids—tri-, tetra-, and penta-, will exist in the solution after some time. Thiosulfuric acid reacts with trithionic
acid to form tetra- and pentathionic acids.

W. Spring (313) said that dilute sulfuric acid is without action in the cold.

A. Longi and L. Bonavia (314) said that potassium permanganate in alkaline solution slowly oxidizes trithionates to sulfate. F. Raschig (315) said that in acidic solution two-thirds of the trithionate goes to sulfate and the remainder to dithionate.

10. Tetrathionic Acid

Tetrathionic acid or the tetrathionates are most easily prepared by the action of iodine on sodium thiosulfate:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

Tetrathionic acid, $H_2S_4O_6$, has never been isolated—it exists only in aqueous solution, this solution having about the same stability as dithionic acid. The concentrated solution, according to M. J. Fordos and A. Gelis (316) decomposes into sulfur, sulfur dioxide, and sulfurous acid.

H. Debus (317) showed that an aqueous solution of potassium tetrathionate at $16^\circ$ slowly decomposes into pentathionate and trithionate, sulfurous acid, and potassium sulfate according to the following reactions:

$$2K_2S_4O_6 = K_2S_8O_6 + K_2S_2O_6$$
$$3K_2S_4O_6 = 2K_2SO_4 + 2SO_2 + K_2S_2O_6$$

A. Sander (318) showed that the presence of thiosulfate accelerated the decomposition of trithionate by
a purely catalytic effect.

Other oxidizing agents besides iodine can produce tetrathionate when acting on sodium thiosulfate. M. J. Fordos and A. Gelis (319), F. Dienert and F. Wandenbulcke (320), and G. Lunge (321) observed that this occurs with hypochlorites.

Fordos and Gelis said that the reaction with chlorates will yield tetrathionate.

E. Sonstadt (322) gives the reaction with iodates as:
\[ 6\text{Na}_2\text{S}_3\text{O}_8 + \text{KIO}_3 + 6\text{HCl} = 5\text{Na}_2\text{S}_4\text{O}_6 + \text{KI} + 6\text{NaCl} + 3\text{H}_2\text{O} \]

A. Nabl (323) gives the reaction with hydrogen peroxide;
\[ 2\text{Na}_2\text{S}_3\text{O}_8 + \text{H}_2\text{O}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaOH} \]
provided the alkali formed is neutralized; otherwise, the tetrathionate is decomposed yielding thiosulfate, sulfate, and sulfite.

H. Marshall (324) observed that thiosulfates are oxidized to tetrathionates by persulfates:
\[ 2\text{SrS}_2\text{O}_8 + \text{K}_2\text{S}_2\text{O}_8 = 2\text{SrSO}_4 + \text{K}_2\text{S}_4\text{O}_6 \]

A. Villiers (325) showed that when sulfur dioxide is passed into a solution of sodium thiosulfate, tetrathionate is formed along with tri- and pentathionates.

W. Spring (326) said that tetrathionate is formed by the action of sulfur monochloride or sulfur dichloride on potassium thiosulfate, and H. Debus (327), by the action of sulfur dioxide and water on sulfur monochloride, hydrochloric, sulfuric, and pentathionic acids and sulfur.
being formed at the same time.

P. Pierron (329) obtained tetrathionicate as a product of the anodic oxidation of sodium thiosulfate.

The formation of tetrathionic acid in the reaction of hydrogen sulfide and sulfurous acid has been discussed under The Polythionates. W. Spring (329) represented the reactions:

\[
\begin{align*}
SO_3 + 2H_2S &= 2H_2O + 3S \\
SO_3 + H_2O + S &= H_2S_2O_3 \\
SO_3 + H_2S_2O_3 &= H_2SO_3 + H_2S_2O_4
\end{align*}
\]

H. Debus (330) said that only \textit{in situ nascendi} will sulfur react with sulfur dioxide.

G. Chancel and E. Diacon (331) state that tetrathionic acid is formed by the spontaneous decomposition of pentathionic acid.

H. Bassett and R. G. Durrant (332) studied the hydrolysis of tetrathionic and pentathionic acids and stated that trithionate is always formed at least as an intermediate product. This occurs by direct decomposition:

\[
\begin{align*}
H_2S_2O_6 &\iff H_2S_4O_6 + S \\
H_2S_4O_6 &\iff H_2S_3O_6 + S
\end{align*}
\]

We may have secondary reactions arising from reaction with sulfurous acid produced by hydrolysis of trithionic acid:

\[
\begin{align*}
H_2S_4O_6 + H_2SO_3 &\iff H_2S_3O_6 + H_2S_2O_3 \\
H_2S_3O_6 + H_2SO_3 &\iff H_2S_2O_6 + H_2S_2O_3 \\
H_2SO_3 + S &\iff H_2S_2O_3
\end{align*}
\]
It is probable that the decompositions of tetrathionic and pentathionic acids are bimolecular:

\[ 2H_2S_3O_6 \rightleftharpoons 2H_2S_4O_6 + S \]
\[ 2H_2S_4O_6 \rightleftharpoons 2H_2S_3O_8 + S \]

The final products of the hydrolysis of trithionic, tetrathionic, and pentathionic acids are sulfuric acid, sulfur dioxide, and sulfur.

The hydrolyses in alkaline solution are symbolized by A. Kurenbach and N. Kaufmann (335) by:

\[ 2H_2S_3O_6 + 3H_2O \rightleftharpoons H_2S_2O_3 + 4H_2SO_3 \]
\[ 2H_2S_4O_6 + 3H_2O \rightleftharpoons 3H_2S_2O_3 + 2H_2SO_3 \]
\[ 2H_2S_3O_8 + 3H_2O \rightleftharpoons 5H_2S_2O_3 \]

A. Sander (334) gives as the reaction of tetrathionate with hydrogen peroxide:

\[ Na_2S_4O_6 + 7H_2O + 6NaOH = 4Na_2SO_4 + 10H_2O \]

Oxidizing agents like chlorine convert the tetrathionate to sulfate according to M. Berthelot (335).

G. S. Jamieson (336) represented the reaction with iodates:

\[ 2Na_2S_4O_6 + 7KIO_3 + 10HCl = 4H_2SO_4 + 2Na_2SO_4 + 2K_2SO_4 \]
\[ + 7ICl + 3KCl + H_2O \]

According to H. Debus (337), sulfur in status nascendi converts the tetrathionates into pentathionates.

V. Lewes (338) found that thiosulfate is produced by the action of hydrogen sulfide on a solution of potassium tetrathionate:

\[ K_2S_4O_6 + 3H_2S = K_2S_3O_8 + 3H_2O + 5S \]
W. Smith and T. Takamatsu (339) said that potassium sulfide reacts with tetrathionate forming thiosulfate:

\[ K_2S_4O_6 + K_2S = 3K_2S_2O_3 \]

H. Debus found that tetrathionic acid is reduced by sulfur dioxide forming sulfur and trithionic acid. The sulfur produces thiosulfuric acid which instead of precipitating sulfur on standing gives half its sulfur to the trithionic acid or the undecomposed tetrathionic acid so as to form tetrathionic or pentathionic acid.

A. Colefax (340) said that sulfite removes sulfur from tetrathionate with the formation of thiosulfate and trithionate:

\[ M_2S_4O_6 + Na_2SO_3 ⇌ M_2S_2O_3 + M_2S_2O_6 \]

F. Raschig (341) found that an acidified solution of sodium thiosulfate converts tetrathionates into pentathionates.

According to W. J. Fordos and A. Gellis (342), nitric acid oxidizes tetrathionates to sulfate with the separation of sulfur. They also state that an excess of potassium hydroxide reacts as follows:

\[ 2K_2S_4O_6 + 3KOH = 2K_2S_2O_3 + 2K_2SO_3 + 3H_2O \]

A. Gutman (343) found that with 1:1 alkali:

\[ 3Na_2S_4O_6 + 12NaOH = 3Na_2S_2O_3 + 5Na_2SO_3 + Na_2S + 6H_2O \]

A. Longi and L. Bonavia (344) found that the tetra-thionates are oxidized slowly by an alkaline solution of potassium permanganate.
II. Pentathionic Acid

H. W. F. Wackenroder (545) proposed the probable formation of pentathionic acid by the action of hydrogen sulfide on a solution of sulfurous acid. The resulting solution is really a mixture of polythionic acids as previously discussed.

C. Ludwig (346) obtained pentathionic acid by the action of hydrogen sulfide on sulfurous acid.

G. Chancel and E. Diacon (347) observed that pentathionic acid is formed when acids act on thiosulfates.

F. Raschig (348) said that pentathionic acid resulted from the action of an acidified solution of thiosulfate on tetrathionates.

W. Petzold (349) stated that pentathionic acid resulted from the polymerization of thiosulfates in acid solutions:

\[ 5S_2O_3^2- + 10 H^+ = 2S_2O_6^{3-} + 4H^+ + 5H_2O \]

H. Bassett and R. G. Durrant (350) give:

\[ Na_2S_4O_6 + Na_2S_2O_3 + 4HA = H_2S_6O_6 + 4NaA + H_2O + SO_2 \]

W. J. Forcós and A. Gelis (351) say that pentathionic acid is formed when water acts on sulfur mono- or dichlorides:

\[ 5S_2Cl_2 + 6H_2O = 5S + 10HCl + H_2S_6O_6 \]

Pentathionic acid is known only in aqueous solution and gradually decomposes giving tetra- and trithionic acids and sulfur. The presence of acids makes it more stable. Any alkaline reagent causes immediate precipitation of sulfur.
H. W. F. Wackenroder (352) found that chlorine and hypochlorous acid oxidize pentathionic acid to sulfuric acid.

M. Berthelot (353) said that bromine oxidizes pentathionates to sulfates. F. Raschig (354) found that a mixture of hydrochloric acid and potassium chlorate oxidizes pentathionic acid to sulfuric acid.

H. Debus (355) gives for the reaction of hydrogen sulfide:

$$H_2S_8O_6 + 5H_2S = 6H_2O + 10S$$

$$3K_2S_8O_6 + 3H_2S = K_2S_2O_3 + 2K_2S_2O_5 + 3H_2O + 10S$$

Debus also showed that an excess of sulfur dioxide transforms a portion of the solution of the acid into tetrathionic or trithionic acid, and part remains undecomposed, while pentathionates are completely transformed into trithionates and thiosulfates; with neutral solutions of sulfites some sulfur dioxide and sulfur are formed.

According to M. J. Fordos and A. Gelis (356) an excess of alkali hydroxide immediately decomposes pentathionic acid:

$$2K_2S_8O_6 + 6KOH = 5K_2S_2O_5 + 3H_2O$$

F. Raschig (357) said that pentathionic acid is slowly oxidized by an acid solution of potassium permanganate.

There is no test applicable for pentathionic acid in aqueous solution. Colloidal sulfur will give the same test as pentathionate.
12. Hexathionic Acid

The existence of hexathionic acid as a chemical individual is doubtful, for it is most probably pentathionic acid mixed with colloidal sulfur.

However, E. Weitz and F. Achterberg (358) claim to have prepared it by the action of potassium nitrite on potassium thiosulfate in the presence of acid and when well cooled.

Hexathionic acid is less stable than pentathionic acid and readily decomposes yielding sulfur and other polythionic acids.

Most of the reactions in which it is claimed to have occurred contain sodium thiosulfate as one of the reactants.

13. Pyrosulfurous Acid

The hypothetical pyrosulfurous acid, \( \text{H}_2\text{S}_2\text{O}_3 \), has not been prepared, but a few of its salts, pyrosulfites, have been prepared by J. S. Muspratt (359), E. Carey and F. Hurter (360), C. Schultz-Sellack (361), and others.

When treated with acid, the pyrosulfites furnish sulfuric acid; and when heated, A. H. Rohrig (362) and M. Berthelot (363) represented the decomposition:

\[
2\text{R}_2\text{S}_2\text{O}_3 = 2\text{R}_2\text{SO}_4 + S + \text{SO}_2
\]

A. Geuther (364) said that some thiosulfate is formed as an intermediate product, but E. Divers (365) did not agree with this.
When sulfur dioxide in excess is passed into a concentrated aqueous solution of sodium carbonate, crystals of sodium pyrosulfite, Na$_2$S$_2$O$_8$, are deposited as the solution cools.

C. Schultz-Sellack (366) found that the salt gradually loses sulfur dioxide when exposed to air, and it passes into normal sodium sulfate.

In general, pyrosulfites are unstable in solution.

14. Disulfuric Acid

The persulfuric acids may be eliminated due to the conditions under which they usually arise. They usually occur in fuming sulfuric acid.

15. Pyrosulfuric Acid

Pyrosulfuric acid, H$_2$S$_2$O$_7$, is usually formed at high temperatures and in the absence of water.

In the presence of water pyrosulfuric acid yields sulfuric acid; and its salts in moist air soon form solutions of hydrosulfate.

16. Sulfur Chlorides

In 1782, A. Hagemann (367) observed that sulfur unites chemically with chlorine, and T. Thompson in 1804 (368) and A. B. Berthellet (369) in 1807 observed that sulfur monochloride, S$_2$Cl$_2$, is formed. F. Donny and J. Mareska (370) found that powdered sulfur absorbs chlorine
at ordinary temperatures and even at temperatures as low as -90° with the evolution of heat. They also found that the absorption is faster if the sulfur be sublimed into chlorine gas.

Four sulfur chlorides have been reported: sulfur tetrachloride, SCl₄; sulfur dichloride, SCl₂; trisulfur tetrachloride, S₃Cl₄; and sulfur monochloride, S₄Cl₂. The latter, sulfur monochloride, is the most common of the four, sulfur dichloride occurring usually at high temperatures, and the identity of the other two as distinct compounds seems to be somewhat doubtful.

According to J. J. Berzelius (371), H. Rose (372), and R. F. Marchand (373), sulfur monochloride is produced by the action of chlorine on sulfur, or on a metal sulfide as indicated in the patent process of the Consortium fur elektrochemische Industrie; or, of sulfur on a metal chloride such as stannous or mercuric chloride. E. Legeler (374) used iodine, iron, or iron chloride as catalysts.

R. Weber (375) found sulfur monochloride as one of the products of the reaction between carbon disulfide and chlorine (best carried out in the presence of iodine as a catalyst):

\[
CS₂ + 3Cl₂ = CCl₄ + S₃Cl₂
\]

H. Goldschmidt (376) observed that the monochloride is formed by the action of phosphorous pentachloride on sulfur:

\[
S₂ + PCl₅ = PCl₃ + S₃Cl₂
\]
and E. Baudimont (377) and G. Chevrier (378) obtained it by the action of phosphorus pentachloride on metal sulfides; by heating thiophosphoryl chloride in sealed tubes to redness; or, by the action of chlorine on thiophosphoryl chloride; L. Carius (379) by heating thionyl chloride with phosphorus sulfide; H. Prinz (380), by heating thionyl chloride with sulfur to 180°; and A. Besson (381) by the action of hydrogen sulfide on sulfuryl chloride.

Sulfur monochloride appears as a yellowish-red, heavy liquid, which fumes in air; it has a disagreeable suffocating odor which has been likened to sea weed; its vapor excites tears; it attacks the mucous membrane; and its taste is said to be sour, hot, or bitter.

On heating to 60° its color darkens considerably and it can be shown that sulfur monochloride undergoes a slight dissociation into sulfur dichloride and sulfur when heated.

T. Thomson (382) observed that the liquid sinks in water and is slowly hydrolyzed into hydrochloric acid, thiosulfuric acid, and sulfur; the thiosulfuric acid also decomposes into sulfurous acid and sulfur so that the initial and final products are:

$$28\text{S}_2\text{Cl}_2 + 3\text{H}_2\text{O} = 4\text{HCl} + \text{H}_2\text{S}_2\text{O}_3 + 3\text{S}$$

C. F. Buchols (383) and H. Rose (384) said that a little sulfuric acid is formed even if the monochloride
contains an excess of sulfur; and M. J. Fordos and A.
Gelis (385) observed that a little pentathionic acid is
formed. L. Carius (386) and H. L. Olin (387) assumed that
the first stage of the hydrolysis furnishes sulfur dioxide
and hydrogen sulfide:

\[ \text{S}_2\text{Cl}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{S} + \text{SO}_3 + 2\text{HCl} \]

which then interact to form thiosulfuric acid, etc. This
equation, according to H. Debus (388), is entirely hypo­
theticical; it is not supported by experiments; and it is
advanced by L. Carius (386) as an argument in favor of his
view of the constitution of the sulfur chlorides.

Sulfur monochloride dissolves in an aqueous solution
of sulfuric acid without the precipitation of sulfur,
but the smallest quantity of hydrogen sulfide, even with
a large excess, produces an immediate precipitate of sul­
fur. The formation of hydrogen sulfide required by Carius's
equation does not, therefore, occur. He, therefore, favored
the former view that water decomposes the monochloride
into thiosulfuric acid, sulfur, and hydrochloric acid:

\[ 2\text{S}_2\text{Cl}_2 + 3\text{H}_2\text{O} = \text{H}_2\text{S}_2\text{O}_3 + 4\text{HCl} + 2\text{S} \]

B. Neumann and E. Fuchs (389), however, considered
that L. Carius's equation represents the course of the
reaction which is followed by a subsequent reaction between
the sulfur dioxide and hydrogen sulfide.

E. Noack (390) said that the end products of the
reaction are the same as in the reaction between sulfurous
acid and hydrogen sulfide; a slight difference in the
amount of sulfuric acid produced in the absence of air is attributed to the oxidizing action of a small quantity of a higher sulfur chloride.

It is assumed that the first stages of the reaction can be represented by:

$$S_2Cl_2 + 2H_2O = S_2(OH)_2 + 2HCl$$

$$S_2(OH)_2 \rightleftharpoons H_2S + SO_2$$

and the presence of sulfur dioxide and hydrogen sulfide can be demonstrated. Attempts to prepare the assumed intermediate compound, $H_2S_2O_3$, however, by the action of hydrogen sulfide on sulfur dioxide in the absence of water, e.g. in alcoholic solution or by passing hydrogen sulfide into liquid sulfur dioxide, failed. The reaction under such conditions proceeds thus:

$$2H_2S + SO_2 = 2H_2O + 3S$$

P. Hautefeuille (391) found that hydriodic acid acts with sulfur monochloride at ordinary temperatures forming hydrochloric acid, iodine, sulfur iodide, and hydrogen sulfide.

T. Thomsen (392) said that nitric acid converts the dichloride into hydrochloric and sulfuric acids with violent everescence.

C. Lowig (393) and M. M. P. Muir (394) observed that nitric acid attacks the monobromide violently forming hydrobromic and sulfuric acids.

G. Korndorfer (395) represented the reaction with a
solution of potassium hydroxide:
\[ 2S_2Br_2 + 6KOH = 4KBr + K_2SO_3 + 3S + 3H_2O \]

H. Rose (396) found that hydrogen sulfide reacts with sulfur monochloride:
\[ S_2Cl_2 + H_2S = 3S + 2HCl \]

17. Thionyl Chloride

A preliminary survey indicates that the occurrence and reactions of thionyl chloride, SOCl₂, eliminate it from consideration in this work. It is usually formed by the action of sulfur dioxide on phosphorous pentachloride and is decomposed by water.

18. Sulfuryl Chloride

Sulfuryl chloride, SO₂Cl₂, is usually formed by the action of sulfur dioxide on chlorine in the presence of a catalyst. It is decomposed by water.

19. Pyrosulfuryl Chloride

Pyrosulfuryl chloride, S₃O₂Cl₂, is formed by the action of sulfur monochloride on sulfur trioxide. Water decomposes it into sulfuric and hydrochloric acids.

20. Chlorosulfonic Acid

Chlorosulfonic acid, ClHSO₃, may be prepared by the interaction of dry hydrogen chloride and sulfur trioxide,
but is decomposed by water yielding sulfuric and hydrochloric acides.

21. Hypochlorous Acid

A. A. Jakowkin (397) gives the following equation as representing the equilibrium between chlorine and water:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl} \]

The presence of hydrochloric and hypochlorous acids have both been established and it has also been shown that in the equilibrium the amounts of the acids is extremely small.

It is argued that an aqueous solution of hypochlorous acid contains the two equilibria:

- \( \text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^- \)
- \( 2\text{HOCl} \rightleftharpoons \text{Cl}_2\text{O} + \text{H}_2\text{O} \)

but an approximately 0.2 N solution contains only about 0.02% chlorine monoxide.

The reaction of chlorine with an aqueous solution of base is represented as follows:

\[ \text{Cl}_2 + 2\text{KOH} \rightleftharpoons \text{KCl} + \text{KOC}1 + \text{H}_2\text{O} \]

As long as the solution contains a slight excess of alkali hydroxide the solution is fairly stable, but in acid solutions we have free hypochlorous acid which is unstable, decomposing as follows:

\[ 2\text{HOCl} \rightarrow \text{HClO}_3 + 2\text{HCl} \]

Decomposition to chlorate occurs to some degree even in basic solution, but is very slow at room temperature.
Heavy metal hypochloriates are so easily hydrolyzed by water that hypochlorous acid may be obtained by merely distilling a solution of the hypochlorite.

P. T. Austen (398) liberated hypochlorous acid from bleaching powder by treating it with sodium bicarbonate.

A. Wohl and H. Schweitzer (399) obtained hypochlorous acid by the action of chlorine on a solution of sodium bicarbonate.

I. Bhaduri (400) found that the decomposition of sodium hypochlorite by heat is a bimolecular reaction at low temperatures:

\[ 2\text{NaOCl} = 2\text{NaCl} + \text{O}_2 \]

and a slight side reaction:

\[ 2\text{NaOCl} = 2\text{NaCl} + \text{NaClO}_3 \]

At higher temperatures the latter is the main reaction.

According to J. Thomsen (401) the heat of neutralization:

\[ \text{NaOH} + \text{HCl} = \text{NaOCl} + \text{H}_2\text{O} \]

is 9.98 Calories.

Hypochlorous acid is so feeble in strength that the carbon dioxide of the air is sufficient to displace the acid from hypochlorites forming carbonates, e.g. P. T. Austen (402) found that a solution of bleaching powder liberates the free acid when treated with sodium hydrogen carbonate, NaHCO\(_3\); and barium carbonate is precipitated from a solution of barium hypochlorite, and hypochlorous acid remains in solution. With an aqueous solution of...
calcium hypochlorite, calcium carbonate is similarly precipitated; chlorine gas is also evolved and some calcium chloride remains in solution.

According to C. F. Schonbein (403) hydrogen peroxide reduces the hypochlorites giving off a volume of oxygen equal to twice that contained in the hypochlorite:

$$\text{KClO}_2 + \text{H}_2\text{O}_2 = \text{KCl} + \text{H}_2\text{O} + \text{O}_2$$

and G. Lunge (404) has used this as a quantitative method for the evaluation of hypochlorites.

When treated with sulfur, hypochlorous acid, or hypochlorites furnish sulfur chloride, chlorine and sulfuric acid; sulfur dioxide gives sulfuric acid and chlorine; hydrogen sulfide not in excess gives sulfuric acid and free chlorine.

F. Dienert and F. Wandenbuleke (405) found that in dilute solution sodium thiosulfate and hypochlorite react:

$$2\text{Na}_2\text{S}_2\text{O}_3 + 5\text{Cl}_2 + 5\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 8\text{HCl} + \text{H}_2\text{SO}_4 + \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaCl}$$

or,

$$5\text{NaOCl} + 3\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O} = 2\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_4\text{O}_6 + 5\text{NaCl} + 5\text{H}_2\text{O}$$

but in the presence of acids, or even sodium hydrogen carbonate, less thiosulfate is used:

$$\text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} = 2\text{NaHSO}_4 + 8\text{HCl}$$

Goldschmidt (406) in a study of the cause of the greater oxidizing power of hypochlorite in acid solution over that in basic solution came to the conclusion that it was due to the presence of chlorine monoxide in the
solution. He was able to prove the presence of chlorine monoxide in aqueous solutions of hypochlorous acid by extraction with carbon tetrachloride. From his results he gives the equilibrium constant for the reaction:

$$2\text{HOCl} \rightleftharpoons \text{Cl}_2\text{O} + \text{H}_2\text{O}$$

as $9.6 \times 10^{-4}$.

Remington and Trimble (407) have shown by potentiometrical measurement that the oxidation potentials of solutions of hypochlorite varied with the pH of the solution, the greater the acidity the greater the oxidation potential and hence the greater the oxidizing power.

Chlorine monoxide and sulfur in the dry state react violently with the formation of sulfur monochloride and sulfur dioxide.
SUMMARY OF THE LITERATURE

1. Oxidation of Sulfides in Solution

(1) The oxidation of hydrogen sulfide results in the formation of sulfur, sulfuric acid, or a mixture of the two. No other product has been shown to result either as an intermediate or final product except in the specific instance of the reaction between hydrogen sulfide and sulfur dioxide, in which case polythionic acids may be shown to exist as intermediate products. However, the formation of polythionic acids is not usually characteristic of oxidation processes, but rather due to the presence of sulfurous acid and nascent sulfur. We may state rather definitely, therefore, that the oxidation of hydrogen sulfide will result only in the formation of sulfur, sulfuric acid, or a mixture of these two.

(2) Sodium sulfide and sodium hydrosulfide yield the following products: $S$, $Na_2S_x$, $Na_2SO_4$, $Na_2S_2O_3$, $Na_2SO_3$, and in some cases polythionates where the alkalinity is limited.

(3) The chief difference in the oxidation of hydrogen sulfide and sodium sulfide lies in the formation of thiosulfate and polythionates. This is no doubt due to the far greater stability of thiosulfate in basic solution. Slightly acid water such as that produced by the solution of carbon dioxide of the air in water possesses sufficient acidity to cause the decomposition of sodium thiosulfate.
Greater acidities cause rapid to immediate decomposition. The appearance of polythionates usually requires the initial presence of thiosulfate or sulfurous acid and nascent sulfur; hence, their absence in acid solution.

(4) In general hydrogen sulfide appears to be more easily oxidized than alkali sulfides.

(5) The ultimate oxidation product of either hydrogen sulfide or sodium sulfide is sulfuric acid regardless of the intermediate products of the reaction. Under the proper conditions any of the other products of the oxidation of sulfide can be ultimately converted to sulfate.

(6) In basic solution the hydroxyl ion has been shown to be an important reactant, whose importance, of course, increases with its concentration. Its action is usually secondary.

(7) Very weak oxidants (certain organic oxidants, e.g. sodium m-nitrobenzene-sulfonate) or slow acting oxidants such as atmospheric oxygen allow a more thorough investigation of the actual mechanism of the reaction through the identification of intermediate products.

(8) A study of such reactions seems to indicate that sulfur is the most probable primary oxidation product of sulfide. In acid solution this may be the only product in the case of weak oxidants, but if a stronger oxidant is present, we may have a partial or complete secondary oxidation of the sulfur to sulfate. In basic solution, in addition to the above possibilities, we have the possibility of the reaction
of sulfur with the hydroxyl ion.

(9) In very rapid reactions there is no possibility of tracing the exact mechanism of the reaction experimentally, but we may postulate mechanisms by analogy with slow reactions. From quantitative information as to concentrations of reactants and products we may be able to limit the possible mechanisms.

(10) The mechanism of the reaction depends upon the acidity or basicity or more generally the pH of the solution.

(11) The extent of oxidation depends fundamentally upon the strength of the oxidant, the specificity of the oxidant, and secondarily upon the temperature.

(12) The study of the oxidation of sulfides in acid solutions is a simpler problem than the corresponding study of oxidation in basic solutions, except where the oxidant is itself influenced by the hydrogen ion concentration.

Reactions of sulfides in solution

<table>
<thead>
<tr>
<th>Sulfide</th>
<th>Reagent</th>
<th>Products</th>
<th>Intermediate</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2S</td>
<td>Air</td>
<td></td>
<td>--</td>
<td>H_2O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H_2SO_4</td>
</tr>
<tr>
<td>NaHS</td>
<td>Air</td>
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<td>--</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Na_2S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Na_2SO_4</td>
</tr>
<tr>
<td>H_2S</td>
<td>H_2O_2</td>
<td></td>
<td>--</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H_2O</td>
</tr>
<tr>
<td>H_2S</td>
<td>H_2O_2(basic)</td>
<td></td>
<td>--</td>
<td>Na_2SO_4</td>
</tr>
<tr>
<td>Sulfide</td>
<td>Reagent</td>
<td>Products</td>
<td>Intermediate</td>
<td>Final</td>
</tr>
<tr>
<td>---------</td>
<td>---------------</td>
<td>---------------------------</td>
<td>--------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>H₂S</td>
<td>HCl</td>
<td>H₂O</td>
<td></td>
<td>H₂SO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂OCl₂</td>
<td></td>
<td>HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂SO₄</td>
<td></td>
<td>Cl₂</td>
</tr>
<tr>
<td>H₂S</td>
<td>HIO₂</td>
<td>H₂O</td>
<td></td>
<td>S</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>I</td>
</tr>
<tr>
<td>H₂S</td>
<td>HBrO₃</td>
<td>H₂O</td>
<td></td>
<td>S</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>Br</td>
</tr>
<tr>
<td>H₂S</td>
<td>NaIO₃</td>
<td>S</td>
<td>H₂O</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>I</td>
</tr>
<tr>
<td>H₂S</td>
<td>NaBrO₃</td>
<td>S</td>
<td>H₂O</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Br</td>
</tr>
<tr>
<td>H₂S</td>
<td>SCl₂OH</td>
<td>S</td>
<td>HCl</td>
<td>H₂SO₄</td>
</tr>
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<td></td>
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<td></td>
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</tr>
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<td></td>
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</tr>
<tr>
<td>H₂S</td>
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<td>S</td>
<td>H₂SO₄</td>
<td>NH₄SO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NO₃</td>
</tr>
<tr>
<td>H₂S</td>
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<td></td>
<td></td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>H₂S</td>
<td>KNO₃</td>
<td>KOH</td>
<td>S</td>
<td>NH₃</td>
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<td></td>
<td></td>
<td>H₂O</td>
</tr>
<tr>
<td>Na₂S</td>
<td>air</td>
<td></td>
<td></td>
<td>Na₂S₂O₃</td>
</tr>
<tr>
<td>Na₂S</td>
<td>Electrolysis</td>
<td>Na₂S₂O₃</td>
<td>S</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na₂S₂</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>Na₂S</td>
<td>KNO₃</td>
<td>Na₂S₂O₃</td>
<td>Na₂S₂</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>Sulfide</td>
<td>Reagent</td>
<td>Products</td>
<td>Intermediate</td>
<td>Final</td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
<td>---------------------------</td>
<td>--------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Na₂S</td>
<td>KMNO₄</td>
<td>--</td>
<td>cold S</td>
<td>Na₂SO₄, Na₂S₂O₅, Na₂S₂O₆</td>
</tr>
<tr>
<td>Na₂S</td>
<td>O₃</td>
<td>--</td>
<td>Na₂SO₄</td>
<td></td>
</tr>
<tr>
<td>Na₂Sₓ</td>
<td>Sodium m-nitrobenzene sulfonate</td>
<td>NaOH</td>
<td>Na₂S₂O₃</td>
<td></td>
</tr>
<tr>
<td>NaHS</td>
<td>O₃</td>
<td>--</td>
<td>Na₂S₂O₃, Na₂SO₃, Na₂SO₄</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>O₂</td>
<td>--</td>
<td>H₂SO₄</td>
<td></td>
</tr>
<tr>
<td>Na₂S</td>
<td>O₂</td>
<td>--</td>
<td>Na₂S₂O₃, Na₂SO₃, Na₂SO₄, Na₂S₂O₅ (?)</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>SO₂</td>
<td>Polythionic acids</td>
<td>S</td>
<td>H₂O</td>
</tr>
<tr>
<td>H₂S</td>
<td>KIO₃</td>
<td>--</td>
<td>S</td>
<td>H₂SO₄</td>
</tr>
</tbody>
</table>

2. Sulfur

(1) At normal temperatures, except in a few specific cases, sulfur appears to be rather resistant to oxidation both by weak oxidants and strong oxidants.

(2) In the absence of moisture the usual product is sulfur dioxide.

(3) In the presence of moisture and when oxidized by slow oxidants the only product is sulfuric acid. Sulfurous acid is probably an intermediate product, but its oxidation to sulfate is apparently more rapid than the initial oxidation.
of the sulfur since it cannot be isolated.

(4) In rapid oxidations, such as with potassium dichromate, sulfite may appear along with sulfate in the final mixture.

(5) The action of iodic acid on colloidal sulfur yielding sulfite, and finally sulfate deserves particular note.

(6) Sulfur is readily attacked by hypochlorous acid yielding sulfur monochloride and sulfuric acid.

(7) Sulfur appears to be more rapidly attacked by solutions of strong bases than it is by oxidizing agents.

(8) In general the rate of the reaction is a function of the surface of the sulfur exposed.

Reactions of Sulfur

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Products</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>--</td>
<td>( \text{SO}_2 )</td>
</tr>
<tr>
<td>Air and Moisture</td>
<td>--</td>
<td>( \text{H}_2\text{SO}_4 )</td>
</tr>
<tr>
<td>( \text{O}_3 )</td>
<td>--</td>
<td>( \text{SO}_2 )</td>
</tr>
<tr>
<td>( \text{O}_3 )</td>
<td>--</td>
<td>( \text{SO}_3 )</td>
</tr>
<tr>
<td>( \text{O}_3 ) and Moisture</td>
<td>--</td>
<td>( \text{H}_2\text{SO}_4 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>--</td>
<td>( \text{H}_2\text{S} ) ( \text{SO}_2 )</td>
</tr>
<tr>
<td>Chlorates</td>
<td>--</td>
<td>( \text{H}_2\text{SO}_4 )</td>
</tr>
<tr>
<td>Bromates</td>
<td>--</td>
<td>( \text{H}_2\text{SO}_4 )</td>
</tr>
<tr>
<td>Iodates</td>
<td>--</td>
<td>( \text{H}_2\text{SO}_4 )</td>
</tr>
<tr>
<td>Perschlorates</td>
<td>No Action</td>
<td></td>
</tr>
<tr>
<td>Periodates</td>
<td>No Action</td>
<td></td>
</tr>
</tbody>
</table>
### Products

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Intermediate</th>
<th>Final</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine Acid (On Colloidal Sulfur)</td>
<td>SO$_2$</td>
<td>H$_2$SO$_4$</td>
<td>Fast</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>No Action</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali Hydroxides (Fused)</td>
<td>Na$_2$S</td>
<td>Na$_2$S$_2$O$_3$</td>
<td>Fast</td>
</tr>
<tr>
<td>* (Excess)</td>
<td>Na$_2$SO$_3$</td>
<td>Na$_2$SO$_4$</td>
<td>Fast</td>
</tr>
<tr>
<td>NaOH Aqueous</td>
<td>Na$_2$S</td>
<td>Na$_2$S$_2$O$_3$</td>
<td>Moderate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Depends upon temperature</td>
</tr>
<tr>
<td>NaNO$_3$ Aqueous</td>
<td>No Action</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$</td>
<td>K$_2$SO$_3$</td>
<td>K$_2$SO$_4$</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>No Action</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3. Sulfurous Acid

1. Sulfurous acid is produced by the action of concentrated acids on sulfites, thiosulfate, and all polythionic acids. It probably also occurs as an intermediate product in the oxidation of sulfur to sulfuric acid in aqueous solution.

2. In general sulfurous acid is oxidized to sulfuric acid and in the same way sulfites to sulfates under the influence of strong oxidizing agents.

3. When treated with weak oxidizing agents polythionic acids may arise.

4. Chlorine and bromine oxidize the acid to sulfuric acid.

5. The salts or sulfites appear to be more easily oxidized than the free acid.
(6) In the presence of sulfur, preferably nascent sulfur, sodium thiosulfate may be formed.
(7) The action of hydrogen sulfide on sulfurous acid gives rise to the very complex mixture known as Wackenroder's liquid, which will be discussed under the polythionic acids. Most of the polythionic acids, as well as sulfur and thiosulfuric acid have been shown to exist in this liquid.

Sulfurous Acid

A. Occurrence in Reactions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intermediate</td>
<td>Final</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>Conc. H₂SO₄</td>
<td>--</td>
</tr>
<tr>
<td>Polythionic</td>
<td>Conc. H₂SO₄</td>
<td>--</td>
</tr>
<tr>
<td>Acids</td>
<td>Electrolysis</td>
<td>--</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₃</td>
<td>Electrolytic</td>
<td>--</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Reduction</td>
<td>--</td>
</tr>
</tbody>
</table>

B. Reactions

<p>| Reagent                    | Products          |
|-----------------            | Intermediate    | Final             |
| Electrolytic Oxidation    | --               | H₂SO₄             |
| Air                        | --               | H₂SO₄             |
| Electrolytic Reduction    | H₂S₂O₄(?)        | H₂S               |
|                            | H₂S₂O₃(?)        |                   |
|                            | H₂S₂O₆(?)        |                   |
|                            | S                |                   |
| Heat                       | --               | S                 |
| Autoxidation               | H₂S₂O₃          | H₂SO₄             |
|                            | Polythionic      | H₂O               |
|                            | Acids            | S                 |
|                            | H₂SO₄            |                   |
|                            | H₂S₂O₄          |                   |</p>
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Intermediate</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>H₂S₂O₃</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Cl₂</td>
<td>--</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Br₂</td>
<td>--</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>I₂</td>
<td>--</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>I₂(NaHSO₃)</td>
<td>--</td>
<td>H₂S₂O₃</td>
</tr>
<tr>
<td>S(Na₂SO₃)</td>
<td>--</td>
<td>Na₂S₂O₃</td>
</tr>
<tr>
<td>HBrO₃</td>
<td>--</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>H₂S</td>
<td>--</td>
<td>H₂S₂O₃</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>--</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>Na₂S</td>
<td>--</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>HNO₂</td>
<td>--</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>HNO₃</td>
<td>No action</td>
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</tr>
<tr>
<td>KMnO₄</td>
<td>--</td>
<td>Na₂SO₄</td>
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<td>K₂MnO₄</td>
<td>--</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Acid</td>
<td>--</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>O₃</td>
<td>--</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Na₂O₂</td>
<td>--</td>
<td>Na₂SO₄</td>
</tr>
</tbody>
</table>

4. Sulfuric Acid

Sulfuric acid occurs as the final oxidation product of various sulfur compounds, and it appears that, once formed, its further reaction is highly improbable.
Sulfuric Acid

A. Occurrence in Reactions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Intermediate</td>
</tr>
<tr>
<td>S</td>
<td>Cl₂, HOCl,</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>HNO₃ and</td>
<td></td>
</tr>
<tr>
<td></td>
<td>KClO₃, H₂O₂</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>H₂O₂, Halogens</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>HOCl, HNO₃</td>
<td></td>
</tr>
<tr>
<td>Metal Sulfides</td>
<td>Electro-</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>oxidation</td>
<td></td>
</tr>
</tbody>
</table>

(For further occurrence see under individual compounds)

B. Reactions

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Conditions</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₃</td>
<td>Conc. H₂SO₄</td>
<td>H₂SO₃</td>
</tr>
<tr>
<td>S</td>
<td>Heated, 200°</td>
<td>SO₂</td>
</tr>
<tr>
<td>H₂S</td>
<td>Conc. H₂SO₄</td>
<td>H₂O, S, H₂SO₄</td>
</tr>
</tbody>
</table>

5. Thiosulfuric Acid

(1) Thiosulfates may result from the action of bases on sulfur, sulfides on sulfurous acid, sulfur on sodium sulfite, atmospheric or electrolytic oxidation of sulfides or polysulfides, and finally by the decomposition of tri-, tetra-, and pentathionates.

(2) Thiosulfuric acid and the thiosulfates are comparatively
easily oxidized. Strong oxidants yield sulfate; weak oxidants yield tetrathionate. Ozone specifically yields a mixture of sulfate and dithionate.

(3) The reaction between thiosulfate and sulfurous acid yields a mixture of tri-, tetra, and pentathionate.

(4) The reaction between hydrogen sulfide and thiosulfurous acid yields sulfur and water.

(5) Thiosulfates are unstable in acid solution yielding sulfur and sulfurous acid.

**Thiosulfuric acid**

**A. Occurrence in Reactions**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Intermediate</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>Ca(OH)$_2$</td>
<td>CaS</td>
<td>CaS$_2$O$_3$</td>
</tr>
<tr>
<td>H$_2$SO$_3$</td>
<td>Na$_2$S</td>
<td>--</td>
<td>Na$_2$S$_2$O$_3$</td>
</tr>
<tr>
<td>Na$_2$SO$_3$</td>
<td>S</td>
<td>--</td>
<td>Na$_2$S$_2$O$_3$</td>
</tr>
<tr>
<td>Ca(HS)$_2$</td>
<td>Air</td>
<td>--</td>
<td>CaS$_2$O$_3$</td>
</tr>
<tr>
<td>S</td>
<td>NaOH</td>
<td>--</td>
<td>Na$_2$S$_2$O$_3$</td>
</tr>
<tr>
<td>NaHS</td>
<td>NaHSO$_3$</td>
<td>--</td>
<td>Na$_2$S$_2$O$_3$</td>
</tr>
<tr>
<td>Na$_2$S$_4$O$_4$</td>
<td>Na$_2$S</td>
<td>--</td>
<td>S</td>
</tr>
<tr>
<td>Na$_2$S</td>
<td>Electrolytic</td>
<td>Na$_2$S$_2$O$_3$</td>
<td>Na$_2$SO$_4$</td>
</tr>
<tr>
<td>Na$_2$S$_x$</td>
<td>Air</td>
<td>--</td>
<td>Na$_2$S$_2$O$_3$</td>
</tr>
<tr>
<td>Na$_2$S</td>
<td>Na$_2$SO$_3$ + I</td>
<td>--</td>
<td>Na$_2$S$_2$O$_3$</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_6$</td>
<td>Hydrolysis</td>
<td>--</td>
<td>Na$_2$S$_2$O$_3$</td>
</tr>
</tbody>
</table>
### B. Reactions

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Intermediate</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH + O₂</td>
<td></td>
<td>K₂SO₄</td>
</tr>
<tr>
<td>Acids</td>
<td>H₂S₂O₆</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>O₃</td>
<td></td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>H₂SO₃</td>
<td>Na₂S₄O₄</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td></td>
<td>Na₂S₂O₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na₂S₂O₆</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td></td>
<td>Na₂S₂O₄</td>
</tr>
<tr>
<td>Cl₂, Br₂</td>
<td></td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>NaOCl</td>
<td></td>
<td>NaHSO₄</td>
</tr>
<tr>
<td>KClO₃ (Acid)</td>
<td></td>
<td>Na₂S₂O₄</td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td>S</td>
</tr>
<tr>
<td>H₂SO₃</td>
<td></td>
<td>K₂S₂O₆</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K₂S₂O₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K₂S₂O₅</td>
</tr>
<tr>
<td>HNO₃</td>
<td></td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Aqua Regia</td>
<td></td>
<td>H₂SO₄</td>
</tr>
</tbody>
</table>

### 6. Sulfoxylic Acid

(1) Sulfoxylic acid, considered as the parent substance of organic sulfoxylates and sulfinates, is entirely a hypothetical compound which has never been isolated. Any postulates, therefore, as to its reactions and occurrence are lacking in experimental proof, and can be arrived at only by analogy and a consideration of the laws of kinetics.
(2) From a consideration of its mode of preparation and general instability, it is the opinion of the author that it may be eliminated as a factor in this work.

7. Hyposulfurous Acid

(1) Hyposulfurous acid usually arises from the reduction of sulfurous acid with weak reducing agents.

(2) This reduction may be effected by hydrogen sulfide and sodium sulfide.

(3) The acid is very unstable decomposing into thiosulfate and sulfite.

(4) The hyposulfites are readily oxidized, the principle oxidation product being sulfate even with weak oxidants. Sulfite may be formed with extremely mild oxidants.

(5) The acid or its salts do not react with sulfur or sulfides but will react vigorously with the polysulfides to form thiosulfate.

### Hyposulfurous Acid

#### A. Occurrence in Reactions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S$_2$O$_3$</td>
<td>Fe (H$_2$)</td>
<td>H$_2$S$_2$O$_4$</td>
</tr>
<tr>
<td>H$_2$S$_2$O$_3$</td>
<td>Electrolysis</td>
<td>H$_2$S$_2$O$_4$</td>
</tr>
<tr>
<td>H$_2$S$_2$O$_3$</td>
<td>H$_2$S</td>
<td>H$_2$S$_2$O$_4$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intermediate</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S$_2$O$_4$</td>
<td>H$_2$S$_2$O$_4$</td>
</tr>
<tr>
<td>H$_2$SO$_3$</td>
<td>H$_2$S$_2$O$_4$</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>H$_2$S$_2$O$_4$</td>
</tr>
<tr>
<td>H$_2$SO$_5$</td>
<td>H$_2$S$_2$O$_4$</td>
</tr>
<tr>
<td>H$_2$SO$_6$</td>
<td>H$_2$S$_2$O$_4$</td>
</tr>
<tr>
<td>Compound</td>
<td>Reagent</td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_3$</td>
<td>HCOOH</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_3$</td>
<td>Na$_2$S</td>
</tr>
</tbody>
</table>

### B. Reactions

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposes</td>
<td>Na$_2$S$_2$O$_4$ Na$_2$S$_2$O$_3$ NaHSO$_3$</td>
</tr>
<tr>
<td>O</td>
<td>Na$_2$SO$_3$ SO$_3$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>Na$_2$SO$_4$ Na$_2$S$_2$O$_6$</td>
</tr>
<tr>
<td>I</td>
<td>Na$_2$SO$_4$</td>
</tr>
<tr>
<td>KIO$_3$</td>
<td>K$_2$SO$_4$</td>
</tr>
<tr>
<td>S</td>
<td>No Action</td>
</tr>
<tr>
<td>Na$_2$S</td>
<td>No Action</td>
</tr>
<tr>
<td>Na$_2$Sx</td>
<td>NaS.SO.OH NaS.SO$_2$.OH Na$_2$S$_2$O$_3$</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>-- Na$_2$SO$_3$ Na$_2$S</td>
</tr>
</tbody>
</table>

### The Polythionic Acids

(1) The polythionic acids are formed when sulfur dioxide, water, and sulfur in statu nascendi react with one another under different conditions.

(2) These acids have been studied in connection with Wackenroder's liquid (a solution resulting from the action of hydrogen sulfide on sulfurous acid).

(3) This liquid has been shown to contain the following:

1. Sulfur in suspension
8. Colloidal sulfur
9. Sulfuric Acid
4. Trithionic Acid
5. Tetrathionic Acid
6. Pentathionic Acid
7. Hexathionic Acid (?)

(4) The occurrence of the above is explained as follows: When hydrogen sulfide is passed into sulfurous acid most of the hydrogen sulfide reacts with the sulfurous acid forming tetrathionic acid. Sulfurous acid then acts on tetrathionic acid giving trithionic and sulfuric acids. The thiosulfuric acid reacts with the tetrathionate to give pentathionic acid. Now, if hydrogen sulfide be passed in in excess it reacts with tetrathionic acid forming water and sulfur. This sulfur in statu nascendi converts trithionic into tetrathionic acid; tetrathionic into pentathionic acid; and pentathionic into hexathionic acid. Some of the sulfur produced remains in solution as colloidal sulfur and part separates as a suspension. The appearance of sulfuric acid in the solution is thought to be due to atmospheric oxidation of sulfurous acid.

(5) In alkaline solutions all the polythionates except dithionic decompose quickly into thiosulfate and sulfite.

8. Dithionic Acid

(1) Dithionic acid or dithionates usually result from
the oxidation of either sulfurous acid or sodium thiosulfate with very weak oxidants such as the hydroxides of the tervalent iron family.

(2) Once formed the dithionates are comparatively stable. They are not oxidized by hypochlorous acid, and do not react with either hydrogen sulfide or sulfurous acid. They are not decomposed by sodium hydroxide.

Dithionic Acid

A. Occurrence in Reactions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2S_2O_3$</td>
<td>$MnO_2$</td>
<td>$H_2S_2O_5$</td>
</tr>
<tr>
<td>$H_2S_2O_3$</td>
<td>$Fe(OH)_3$</td>
<td>$H_2S_2O_5$</td>
</tr>
<tr>
<td>$H_2S_2O_3$</td>
<td>$K^2MnO_4$</td>
<td>$H_2S_2O_5$</td>
</tr>
<tr>
<td>$H_2S_2O_3$, acidic</td>
<td>Electrolytic Oxidation</td>
<td>$H_2S_2O_5$</td>
</tr>
<tr>
<td>$Na_2S_2O_3$</td>
<td>$H_2O_2$, Neutral</td>
<td>$H_2S_2O_5$</td>
</tr>
<tr>
<td>$Na_2S_2O_3$, $K^2MnO_4$, acidic</td>
<td>$H_2S_2O_5$</td>
<td></td>
</tr>
</tbody>
</table>

B. Reactions

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Na_2O_2$</td>
<td>$Na_2SO_4$ (slow)</td>
</tr>
<tr>
<td>$H_2S$</td>
<td>No Action</td>
</tr>
</tbody>
</table>
9. Trithionic Acid

(1) Trithionic acid and the trithionates can arise from a number of reactions involving as parent substances bisulfite, thiosulfate, sulfide, and polysulfide. Their occurrence in reactions is usually accompanied by the presence of other polythionates.

(2) The acid slowly decomposes at ordinary temperatures with the separation of sulfur, the evolution of sulfur dioxide, and the formation of sulfuric acid.

(3) It is more stable in acid solution but undergoes hydrolysis in acid, neutral, and alkaline solution.

(4) It is oxidized by chlorine to sulfate.

(5) With sulfur it forms tetra- and pentathionate.

(6) It reacts with potassium sulfide to form thiosulfate, but it does not react with hydrogen sulfide.

(7) With sulfur dioxide it forms tetra- and pentathionate.

(8) The reaction with thiosulfate yields tetra- and pentathionate.

Trithionic Acid

A. Occurrence in Reactions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHSO₃</td>
<td>S</td>
<td>K₂S₂O₅</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K₃S₃O₅</td>
</tr>
<tr>
<td>Compound</td>
<td>Reagent</td>
<td>Intermediate</td>
</tr>
<tr>
<td>------------------</td>
<td>---------</td>
<td>--------------</td>
</tr>
<tr>
<td>$\text{K}_2\text{S}_2\text{O}_3$</td>
<td>$\text{SO}_3$</td>
<td>--</td>
</tr>
<tr>
<td>$\text{K}_2\text{S}$ and $\text{KHSO}_3$</td>
<td>$\text{SO}_3$</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Na}_2\text{S}_2\text{O}_3$</td>
<td>$\text{SO}_3$</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Na}_2\text{SO}_3$ and $\text{Na}_2\text{S}_2\text{O}_3$</td>
<td>$\text{I}$</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Na}_2\text{S}_2\text{O}_3$</td>
<td>$\text{H}_2\text{O}_2$ 0-10°C</td>
<td>--</td>
</tr>
<tr>
<td>$\text{Na}_2\text{S}$ or $\text{Na}_2\text{S}_x$</td>
<td>$\text{KMnO}_4$</td>
<td>--</td>
</tr>
<tr>
<td>$\text{K}_2\text{SO}_3$</td>
<td>$\text{S}_2\text{Cl}_2$</td>
<td>--</td>
</tr>
</tbody>
</table>

**B. Reactions**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Intermediate</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis acid</td>
<td>--</td>
<td>$\text{H}_2\text{S}$; $\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>Hydrolysis neutral</td>
<td>--</td>
<td>$\text{H}_2\text{SO}_4$; $\text{H}_2\text{S}_2\text{O}_3$</td>
</tr>
<tr>
<td>Hydrolysis Alkaline</td>
<td>--</td>
<td>$\text{Na}_2\text{SO}_3$; $\text{Na}_2\text{S}_2\text{O}_5$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>--</td>
<td>$\text{Na}_2\text{SO}_4$</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}_2$</td>
<td>--</td>
<td>$\text{Na}_2\text{SO}_4$</td>
</tr>
<tr>
<td>$\text{Cl}_2$</td>
<td>--</td>
<td>$\text{Na}_2\text{SO}_4$</td>
</tr>
<tr>
<td>$\text{HClO}_3$</td>
<td>--</td>
<td>$\text{S}$; $\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>$\text{S}$</td>
<td>--</td>
<td>$\text{K}_2\text{S}_3\text{O}_6$; $\text{K}_2\text{S}_2\text{O}_6$</td>
</tr>
</tbody>
</table>
10. Tetrathionic Acid

(1) Tetrathionate usually results from the partial oxidation of thiosulfate.
(2) It is hydrolyzed both in acid and alkaline solution.
(3) Chlorine oxidizes it to sulfate.
(4) It reacts with nascent sulfur to form pentathionate.
(5) With hydrogen sulfide it yields thiosulfate and sulfur with potassium sulfide, thiosulfate.
(6) It reacts with sodium sulfite to form thiosulfate and trithionate.
(7) In alkaline solution it is decomposed into thiosulfate and sulfite.

### Tetrathionic Acid

#### A. Occurrence in Reactions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>I</td>
<td>Na$_2$S$_4$O$_6$</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>NaOCl</td>
<td>Na$_2$SO$_4$ Na$_2$S$_4$O$_6$</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>NaClO$_2$</td>
<td>Na$_2$S$_4$O$_6$</td>
</tr>
<tr>
<td>Compound</td>
<td>Reagent</td>
<td>Products</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>KIO₃</td>
<td>Na₂S₄O₆</td>
</tr>
<tr>
<td>Na₂S₂O₅</td>
<td>H₂O₂</td>
<td>Na₂S₄O₆</td>
</tr>
<tr>
<td>Na₂S₂O₆</td>
<td>SO₂</td>
<td>Na₂S₄O₆ Na₂S₂O₆ Na₂S₃O₆</td>
</tr>
<tr>
<td>K₂S₂O₃</td>
<td>S₂Cl₂ or SCl₂</td>
<td>Na₂S₄O₆</td>
</tr>
<tr>
<td>S₂Cl₂</td>
<td>SO₂ and</td>
<td>H₂S₄O₆ H₂SO₄</td>
</tr>
<tr>
<td>Na₂S₂O₆</td>
<td>Decomposes</td>
<td>Na₂S₄O₆ S</td>
</tr>
</tbody>
</table>

**B. Reactions**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis Acid</td>
<td></td>
</tr>
<tr>
<td>Hydrolysis Alkaline</td>
<td></td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Na₂S₂O₆ Na₂S₃O₆</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Na₂S₂O₆</td>
</tr>
<tr>
<td>KIO₂</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>S (Nascent)</td>
<td>Na₂S₄O₆</td>
</tr>
<tr>
<td>H₂S</td>
<td>K₂S₂O₃ S</td>
</tr>
<tr>
<td>K₂S</td>
<td>K₂S₂O₃</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>Na₂S₃O₆ Na₂S₅O₆</td>
</tr>
<tr>
<td>KOH (15%)</td>
<td>K₂S₂O₃ K₂SO₃</td>
</tr>
</tbody>
</table>
II. Pentathionic Acid

(1) Pentathionic acid is one of the products of the reaction between hydrogen sulfide and sulfurous acid.
(2) It may result in the acid decomposition of thiosulfate.
(3) Hypochlorous acid oxidizes it to sulfate.
(4) It reacts with hydrogen sulfide to form sulfur, thiosulfate, and trithionate.
(5) It reacts with sulfur dioxide to form tri- and tetra-thionates.
(6) In basic solution it is immediately decomposed yielding thiosulfate.

Pentathionic Acid
A. Occurrence in Reactions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reagent</th>
<th>Products</th>
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<tbody>
<tr>
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<td></td>
<td></td>
<td>H₂SO₄</td>
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<td></td>
<td></td>
<td>H₂S₂O₃</td>
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<tr>
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<td></td>
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<td>Na₂S₂O₄</td>
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<td></td>
<td>and acid</td>
<td>H₂S₂O₆</td>
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B. Reactions

<table>
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<tr>
<th>Reagent</th>
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<td>$SO_2$</td>
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<td>$KOH$</td>
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<tr>
<td>$KMnO_4$</td>
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</table>

16. Sulfur Monochloride

(1) Sulfur monochloride may be formed by the direct action of chlorine on sulfur at temperatures as low as $-90^\circ$.

(2) It can also be formed by other methods which methods, however, do not appear applicable to this problem.

(3) It is slowly decomposed in water yielding as final products sulfur and sulfurous acid. We may have as intermediate products thiosulfuric acid and perhaps pentathionic acid.

(4) The dichloride and monobromide react violently with nitric acid forming sulfuric acid.

(5) Solutions of base transform the monochloride into sulfur and sulfite.

21. Hypochlorous Acid

(1) Hypochlorous acid is formed by the action of chlorine
on water. Hydrochloric and hypochlorous acids are produced and the reaction is represented as an equilibrium but the amounts of the acids present are very small.

(2) The hypochlorites may be produced by the action of chlorine on a solution of an alkali hydroxide. The hypochlorites in basic solution are fairly stable, whereas, hypochlorous acid is quite unstable tending to form chloric acid.

(3) Hypochlorous acid is so feeble in strength that it is released from its salts by sodium bicarbonate.

(4) Hydrogen peroxide completely reduces the hypochlorites.

(5) When treated with sulfur, hypochlorous acid, or hypochlorites furnish sulfur chloride, chlorine, and sulfuric acid.

(6) Sulfur dioxide is oxidized to sulfuric acid.

(7) Hydrogen sulfide not in excess gives sulfuric acid and free chlorine.

(8) At pH values below 8.5 hypochlorites oxidize thiosulfate entirely to sulfate. More basic solutions may yield sodium tetrathionate as an intermediate product.

From the foregoing study of the following compounds it is evident that we may eliminate them as having any bearing on the present work:

Thionyl chloride
Sulfuryl chloride
Chlorosulfonic acid
Pyrosulfuryl chloride
Persulfuric acids
Pyrosulfuric acid
Pyrosulfurous acid
Sulfoxylic acid

We may also eliminate the following compounds for reasons to be discussed latter:

Dithionic Acid
Hexathionic Acid

This leaves the following for more thorough study particularly with respect to their interaction with each other:

Hydrogen sulfide
Sulfur
Sodium sulfide
Sodium polysulfide
Sulfuric Acid
Sulfurous acid
Thiosulfurous acid
Trithionic acid
Tetrathionic acid
Pentathionic acid
Hyposulfurous acid
Sulfur monochloride
Hypochlorous acid

The primary oxidation product of sulfides with any oxidant is probably sulfur. The secondary reactions which may thereafter occur seem to depend upon the factors concentration, hydrogen ion concentration, and the nature of the oxidant. The mechanism is probably affected only by the hydrogen ion concentration.

From the standpoint of mechanism, therefore, it appears to be best to consider the interactions that can occur between the above compounds with respect to the acidity or alkalinity of the solution. The results are given in the following tables.
# Acid Solution

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<tr>
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EXPERIMENTAL WORK

Introduction

Iodimetric methods were used throughout this work in the standardization of sulfide and hypochlorite solutions and in the determination of the oxidizing or reducing power of the various reaction mixtures.

Standard iodine and sodium thiosulfate solutions of suitable concentrations were prepared according to accepted methods (408).

Sodium hypochlorite solutions: Hypochlorite solutions were made by passing chlorine gas into a solution of sodium hydroxide of sufficient strength so that the desired hypochlorite solution would contain a slight excess of base to insure greater stability. The normality of the solution was determined by titration, the iodine liberated from an excess of acidified potassium iodide solution with standard thiosulfate solution. Solutions of approximately the following normalities were used:

0.2
0.1
0.05
0.005

Sodium sulfide solutions: These solutions were made up by dissolving an approximate weight of freshly washed, clear crystals of reagent grade $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in a liter of distilled water. The normality of the sulfide solution was determined by pipetting a portion of the solution into an acidified solution of standard iodine and titrating the
excess iodine with standard thiosulfate solution. Solutions of approximately the following normalities were used:

0.2
0.1
0.05
0.005

The sulfide solutions were found to be unstable and it was necessary to prepare and standardize fresh solutions frequently.

Standard acid and base: In this work it was found necessary to prepare hydrochloric acid and sodium hydroxide solutions of approximate normalities 0.1 and 0.05. They were prepared and standardized in the usual manner.

Benzidine hydrochloride solution: The benzidine hydrochloride reagent for the precipitation of sulfate was prepared according to the method given by Treadwell and Hall (408).

Measurement of pH: The oxidizing and reducing characteristics of all of the solutions used in this study rendered the use of colorimetric indicators, the hydrogen electrode, and the quinhydrone electrode impossible. The glass electrode has recently come into widespread application for use with an ordinary potentiometer circuit because it functions in unbuffered solutions, and has proved itself admirably adapted for the author's purpose. The glass electrode has a range of 0 to 12.5 pH, and a limit of error of 0.1 pH. It is non-poisoning and does not contaminate the solution being tested. The only practical limitations to its use
are that the solution must not be over 0.1 molar in sodium or potassium ion and that it must be free-flowing, without heavy suspended solids. In addition to the glass electrode, the author's circuit included a Leeds and Northrup calomel electrode No. 7724, a Leeds and Northrup Type K-2 potentiometer, and a Leeds and Northrup Type R, No. 2500-b galvanometer having a sensitivity of 0.0005 microampere per millimeter per meter. With this device it was very easy to obtain pH readings on any given solution which checked within 0.05 pH.

1. Concentration Effect

In reviewing the work of Stevens (2), the author was struck by the fact that upon mixing one equivalent of sulfide with one equivalent of hypochlorite, the resulting solution yielded a qualitative test for sulfide. It appeared that this would indicate that sulfide and hypochlorite do not react equivalent for equivalent but that there is rather some reaction mechanism in effect whereby more hypochlorite is required than is indicated by the ratio 1:1.

The first investigation, therefore, was to determine the equivalent reaction ratio between sodium sulfide and sodium hypochlorite, i.e. the number of equivalents of hypochlorite required per equivalent of sulfide.

To carry out this investigation exactly 0.05 N sodium hypochlorite and exactly 0.05 N sodium sulfide solutions
were prepared. It was decided to take a definite quantity of the hypochlorite solution and add to this varying quantities of sodium sulfide solution until the resulting solution showed a qualitative test for sulfide. At the same time the excess oxidizing or reducing power of the solutions was determined iodimetrically. The change in basicity of the solution was determined by titration with standard hydrochloric acid solution. Also, qualitative tests for sulfate were made on each solution.

The results are shown in Table 1. It is seen that, starting with 50 cc. of hypochlorite and adding 5 cc. portions of sulfide, negative tests for sulfide are found until 30 cc. of the sodium sulfide solution have been added. There is a test for sulfate throughout the entire run; colloidal sulfur was also evident. It further appears that there is a steady increase of basicity upon the addition of increasing amounts of sulfide.

It is evident from the above results that there is some mechanism in effect whereby the production of colloidal sulfur and sulfate occurs simultaneously either by some parallel reaction mechanism or by some consecutive mechanism. Hence, it would be expected and was found experimentally that more hypochlorite than sulfide is required. Regardless of the mechanism the following quantitative relationships may be established:

\[
NaOCl + Na_2S + H_2O = S + NaCl + 2NaOH
\]

\[
4NaOCl + Na_2S = 4NaCl + Na_2SO_4
\]
The validity of the first equation is indicated by the fact that there is an increase in basicity as shown in the table. Also there appears to be no possible equation which will show the direct production of sulfur without the simultaneous production of sodium hydroxide. From these results it cannot be definitely stated that sulfur is a primary oxidation product of sulfide; it may be a secondary product arising from the decomposition of some other product produced in the reaction. But, regardless of the actual mechanism, it may be stated that for the production of sulfur from sulfide one equivalent of hypochlorite is required per equivalent of sulfide; and for the production of sulfate, one equivalent of sulfide requires four equivalents of hypochlorite.

It is evident, therefore, that if sulfur were produced exclusively, the following relation would hold:

\[
\frac{\text{Eq. } \text{NaOCl}}{\text{Eq. } \text{Na}_2\text{S}} = 1
\]

and if sulfate were produced exclusively:

\[
\frac{\text{Eq. } \text{NaOCl}}{\text{Eq. } \text{Na}_2\text{S}} = 4
\]

Accordingly, if sulfate and sulfur are produced simultaneously as indicated in Table 1, we would expect the ratio of hypochlorite to sulfide to assume some value between 1 and 4.

From the data in Table 1 we can calculate the ratio of hypochlorite to sulfide when various portions of sulfide are added to a constant quantity of hypochlorite. The results are shown in Table 2. It appears that, except for the first
value, the ratio is fairly constant at about 1.84.

The next obvious step was to investigate the effect of changing concentration on the constancy of the ratio. The ratio was, therefore, determined at the following approximate concentrations, the concentrations of the hypochlorite and sulfide being kept approximately the same:

0.2 N
0.1
0.05

The results are tabulated in Tables 3, 4, and 5 respectively. It is seen that for any given concentration that the ratio is approximately constant, but that there is some variation from one concentration to the other. The results appear to be anomalous since the ratio for the 0.1 N solutions is 1.78 which is lower than the value for either the 0.2 N or the 0.05 N solutions which are respectively, 1.86 and 1.88. However, the reason for this anomaly became apparent later in the study of the effect of pH. In this preliminary work no attempt was made to keep the pH of the solutions at any set value.

It has been assumed that sulfur and sulfate were the only products produced. This is not necessarily an established fact from the data obtained thus far. There are two methods of approach in proving or disproving this assumption. We may make qualitative tests for various compounds which are likely to occur in this reaction or we may make a quantitative determination of the products.
If it is assumed that only sulfur and sulfate are formed in the reaction, we may calculate the quantity of sulfur and sulfate that should exist in any mixture of sulfide with hypochlorite from the ratio of hypochlorite to sulfide since it is known that one equivalent of hypochlorite per equivalent of sulfide is necessary to convert the sulfide to sulfur and four equivalents are necessary to convert it to sulfate. We may arrive at the amount of products produced by taking one mole of sodium sulfide as a basis of calculation and applying the following reasoning. (The ratio for 0.2 N solutions will be used in this example since this was the concentration at which the sulfate content was most readily gravimetrically determined.)

Starting with one mole of sodium sulfide and letting \( x \) moles go to sulfur and \( y \) moles to sulfate, we can obtain two simultaneous equations, one with respect to the sulfide and one with respect to the hypochlorite:

\[
\begin{align*}
\text{Sulfide} & \quad x + y = 1 \\
\text{Hypo} & \quad x + 4y = 1.86
\end{align*}
\]

from which we find

\[
\begin{align*}
x &= 0.7133 \text{ moles sulfur} \\
y &= 0.2867 \text{ moles sulfate}
\end{align*}
\]

Or, we may say that \( x/y \) or \( S/\text{SO}_4 \) = 2.49 which means that at a concentration of our reactants, hypochlorite and sulfide, of 0.2 N the reaction mixture should yield a ratio of sulfur to sulfate of 2.49.
Therefore, to prove the original assumption that only sulfur and sulfate are produced as end products in the reaction, it becomes necessary to devise some analytical method to determine the quantity of either sulfur or sulfate produced in the reaction since the proof of one necessarily proves that the original assumption is correct.

A method for the analysis of sulfate would appear to be more logical than a direct analysis for sulfur, but no method was available which was directly applicable to this system. Inasmuch as the quantity of sulfate to be determined was small the benzidine sulfate method seemed to be the most promising.

The applicability of this method in the determination of the quantity of sulfate arising in the reaction between sodium hypochlorite and sodium sulfide at concentrations of approximately 0.2 N was investigated. Since it was desired to make several determinations, i.e. sulfate produced by the addition of various quantities of sulfide to a set excess of hypochlorite, we calculated the theoretical quantities of sulfate that should be produced and made up known solutions of sulfate containing these quantities and applied the benzidine sulfate method to them.

This method is as follows: The sulfate is precipitated by the addition of an excess of the benzidine hydrochloride reagent to the sulfate solution. The solution is then allowed to stand five minutes and the precipitate filtered off by suction. The filter paper containing the precipitate
is then placed in a stoppered flask with fifty milliliters of water and shaken to a uniform pulp. The contents of the flask are heated to 50° and titrated with standard base to the phenolphthalein end point. The solution is then brought to a boil and the titration completed. The sulfate is calculated from the amount of base required.

The results of this investigation are shown in Table 6. Although some error results, the method appears to be sufficiently exact to indicate with a reasonable degree of accuracy the percent sulfate in our samples.

This method was not directly applicable to the reaction mixture, since it contained besides sulfate, colloidal sulfur and an excess of sodium hypochlorite. The solution was also basic and the method requires that the sulfate be precipitated in a neutral or slightly acid solution.

It became evident immediately that the excess of hypochlorite must be destroyed before addition of the benzidine reagent since hypochlorite was shown to have some action on the reagent whereby it was turned a deep red in color. According to the literature (408) hypochlorite is completely reduced by hydrogen peroxide according to the following equation:

\[ \text{NaOCl} + \text{H}_2\text{O}_2 = \text{NaCl} + \text{H}_2\text{O} + \text{O}_2 \]

This reaction was, therefore, employed in the destruction of the excess hypochlorite by the addition of an excess of hydrogen peroxide. Hydrogen peroxide was shown to have no
action on the benzidine reagent.

However, the solution still contains colloidal sulfur but at this time it was not believed that the sulfur would have any effect on the sulfate determination.

The first method tried was as follows: Titrate the reaction mixture to neutrality with 0.1 N HCl using phenolphthalein as the indicator renewing the phenolphthalein as it is bleached by the hypochlorite. Add a calculated excess of 3% hydrogen peroxide, bring to a boil to coagulate the sulfur, cool to room temperature, add the benzidine reagent and complete the method as outlined above. The results are shown in Table 7. Keeping in mind that the theoretical ratio of sulfur to sulfate should be 2.49, it is seen that the results obtained in this table are unsatisfactory. The sulfate content ran too high which, of course, causes the ratio of sulfur to sulfate to be too low.

The reason for the high sulfate content became evident upon study. It was found in a later investigation that, although the action of sodium hypochlorite on colloidal sulfur to form sulfate is very slow in basic solution, an acidified solution of hypochlorite has a rapid action on colloidal or suspended sulfur. It was therefore, deemed advisable to destroy the hypochlorite before acidification by the addition of an excess of hydrogen peroxide to the basic solution, and then acidify.

This modification was included in the original method and the results are shown in Table 8. Again it was found
that the sulfate content ran higher than was expected, but in this case it was found that, even after the addition of hydrogen peroxide in a calculated excess, the solution still contained an excess of hypochlorite as evidenced by the fact that there was some discoloration on the addition of the benzidine reagent. The results in this table are, therefore, inconclusive. Hydrogen peroxide is so unstable in basic solution that part of it was decomposed before reaction with the hypochlorite.

It was then thought that if we immediately acidified by adding the calculated quantity of acid and then immediately added the peroxide, the hypochlorite could be destroyed before it had any action on the colloidal sulfur, but this method again gave unsatisfactory results as is shown in Table 9.

In all of the above discussed cases it is seen that the sulfate ran high, the difficulty being the destruction of the excess hypochlorite in such a manner that at the same time it was not put in such a favorable condition to act on the sulfur.

We next devised the scheme of mixing the calculated quantity of acid with the hydrogen peroxide and then adding the mixture to the solution. If, in this case, the reaction of hypochlorite with hydrogen peroxide is faster than it is with colloidal sulfur, we should be able to get an accurate determination of the sulfate content. A preliminary investi-
igation of this method indicated that it would give fairly satisfactory results. We, therefore, decided to check the reliability of the method by comparison of the results on several identical solutions.

The results are shown in Table 10 and the checks are excellent considering the exigencies of the method. It was further found here that it was unnecessary to boil the solution before filtering off the sulfur since with the above treatment, it was found that the sulfur was in such a condition that it could be completely filtered out through a double Wattman No. 40 filter paper. However, it appeared to make no difference whether the solution was boiled or not. Solutions 1, 2, and 3 were boiled before filtering off the sulfur while solution 4 was filtered without boiling. The results are practically the same.

Even these last results, however, show some excess of sulfate since we have not yet attained the theoretical ratio of 2.49, but the author was inclined to believe here that since we were dealing with very small quantities of sulfate that this excess was due to contamination of one of the reagents used. All of the solutions used gave negative tests for sulfate except the hydrogen peroxide which gave a slight test.

The amount of sulfate contained in a given portion (that portion which was used to neutralize the hypochlorite in Table 10) was determined. The results are recorded in Table 11 in cc.'s of base required since the correction was
applied directly to the total co.'s of base required in Table 10.

The corrected values for the ratio of sulfur to sulfate from Table 10 are given in Table 12 and it is evident that there is a fairly close check with our postulated ratio.

At this time it was found, however, that in some of the solutions where there was a considerable excess of hypochlorite, too large a volume of 3% hydrogen peroxide was required for reaction with the hypochlorite. It was decided to use 30% hydrogen peroxide in future determinations. (It has been shown in the literature that hydrogen peroxide has no effect on finely divided sulfur (60)).

The determination of the sulfate content of 30% hydrogen peroxide per ten cc. is shown in Table 13. It was found that 10 cc. of hydrogen peroxide was sufficient to destroy the hypochlorite in all of the solutions used; accordingly, it was used in this constant amount at all times to simplify calculations.

The original determinations of the sulfate formed when varying quantities of sulfide are added to a constant excess of hypochlorite were repeated using the method as finally worked out in the above discussion. Table 14 shows that there is obtained an average value of about 2.40 versus the calculated value of 2.49 which is a reasonable check considering the error which may occur in the originally
determined ratio of hypochlorite to sulfide which may be in error at times as much as one or two percent due to the obscuring effect of colloidal sulfur in the iodimetric titrations. Note should also be made that any error made in the original ratio will be doubled in the final ratio of sulfur to sulfate.

From the above results it seems, therefore, that the only products which exist in the final reaction mixture are sulfur and sulfate and that they may be determined from the ratio of the initial reactants sulfide and hypochlorite, under any given set of conditions.

Hence, further study was confined entirely to the volumetric determination of the ratio of sulfide to hypochlorite since it offered a much more rapid method than the corresponding gravimetric study.

It will be noted that the foregoing work has been a study of the reaction at various concentrations but that in all cases the concentrations of the sulfide and hypochlorite solutions have been approximately the same.

We were interested to find out if the ratio of the reactants would be materially changed if the concentrations of our reactants were different from each other; we, therefore, began a series of investigations which may be divided into two parts:

1. Sulfide more concentrated than hypochlorite
2. Hypochlorite more concentrated than sulfide
For the first, the experimental work was as follows: To an excess of hypochlorite solution sulfide of various concentrations was added and the excess hypochlorite determined by addition of acidified potassium iodide solution and titration of the iodine liberated with standard sodium thiosulfate solution. From this we could calculate the ratio of hypochlorite to sulfide at various sulfide solution concentrations. The results are tabulated in Table 15. It is evident at least in a qualitative way that in general the ratio of hypochlorite to sulfide decreases with increase of sulfide concentration showing that formation of sulfur is favored.

At this time the author became conscious of another effect, i.e. the rate of addition of the sulfide to the hypochlorite. The results are shown in Table 16. Using sulfide and hypochlorite solutions of the concentrations as shown in the table the method was as follows:

First, 5 cc. of the sulfide solution was added as rapidly as possible from a burette to 100 cc. of the hypochlorite solution and the residual oxidizing power determined as usual.

Second, 5 cc. of the sulfide solution were added slowly (total time required 200 seconds) to 100 cc. of the hypochlorite solution and the oxidation power of the resulting solution determined.

It is evident from the table that slow addition favors the formation of sulfate. This, of course, is just another
method of changing the relative concentrations of the reactants at any given time.

The rate of addition appeared to be of minor importance where the concentrations of the reactants were approximately the same.

Table 17 shows the effect of addition of hypochlorite to sulfide in which there is an excess of sulfide until the reaction is complete. This process gave a lower ratio than either of the foregoing.

Table 18 shows the effect of the addition of various quantities of sulfide to a definite excess of hypochlorite where the concentrations of the hypochlorite and sulfide are widely divergent. It is seen that the ratio in this case is not even approximately constant as is the case when the hypochlorite and sulfide are of the same concentration but follows the same general trend as has been indicated in the above concentration effect.

We next investigated the effect of having a greater concentration of hypochlorite over that of the sulfide and the results are tabulated in Table 19. The ratio here increases to a maximum of almost 3 showing that increase in concentration of hypochlorite with respect to sulfide concentration increases the formation of sulfate.

In rounding out the study of the effect of concentration on the reaction of hypochlorite with sulfide in basic solution it was deemed advisable to investigate the possi-
hility of the effect of excess hypochlorite on colloidal sulfur and the effect of sodium hydroxide on colloidal sulfur.

Table 20 shows that the rate of reaction of hypochlorite on colloidal sulfur is very slow. The rate was studied by the disappearance of the hypochlorite as determined by addition of acidified potassium iodide solution and titration of the iodine set free at different times. The results are expressed in cc.'s of standard thiosulfate. This reaction then cannot have any influence on the gravimetric determinations of sulfate as previously discussed since the excess hypochlorite was destroyed within one or two minutes after the formation of the colloidal sulfur and it is seen in the table that there is no appreciable action until about twenty minutes has elapsed.

Sodium hydroxide is known to react with sulfur even at ordinary temperatures but the rate of the reaction is very slow. However, we desired definite information in regard to this reaction at room temperature and also at various concentrations of base. The results are shown in Tables 21, 22, and 23.

The method in Table 21 was as follows: From the foregoing determinations of the ratio of hypochlorite to sulfide we mixed as nearly equivalent quantities of sulfide and hypochlorite as possible and added a very slight excess of sulfide to insure complete elimination of hypochlorite. No further addition of base was added
to this solution since we wished to determine the action of the base produced by the reaction itself. The solution had a basicity of 0.0308 N as determined by titration with standard acid. The course of the reaction can be followed by titration of the increase in reducing power since sulfur and sodium hydroxidie react as follows:

$$6\text{NaOH} + 3\text{S} = 3\text{Na}_2\text{S} + \text{Na}_2\text{S}_3\text{O}_3 + 3\text{H}_2\text{O}$$

The reducing power at any time may be determined by pipetting a portion of the solution into an excess of acidified iodine solution and back titrating the iodine with thiosulfate.

The results show that the action is very slow with the basicity above mentioned. Note should be made that the cc.'s of iodine reduced are reported as cc.'s of 0.01 N iodine while the original solutions were 0.1 N. Accordingly, a better insight into the actual proportion of sulfur reacting can be seen by division of the cc.'s of iodine by ten.

Table 22 shows the rate of the reaction when the solution is made 1 N with respect to base and we find a considerable increase in the rate.

Table 23 with a basicity of 2 N seems to have a slower action on sulfur than does a 1 N solution.

However, the results are more or less meaningless from a quantitative point of view since there are too many factors at play to expect any consistent results.
The inconsistency of the results is shown by a comparison of Tables 23 and 24 both of which were run in 2 N basic solution. There is a coagulation of the colloidal sulfur and finally a precipitation in these solutions, the rate of coagulation and precipitation depending upon the concentration of electrolyte present, so no definite conclusion can be reached except the qualitative statement that the rate is too slow to affect the previous determinations which, of course, was our original intention.

In concluding this portion of the investigation, we checked the results of Sgevens (2) and Johnson (3) in acid solution, i.e. quantitative conversion of sulfide to sulfate. The results are given in Tables 25 and 26 at concentrations of approximately 0.1 N and 0.05 N respectively. The experimental ratio is shown to lie very close to the theoretical ratio of 4.

In the above it was found that if the sulfide were added at a moderate rate, colloidal sulfur never became apparent in the solution. However, if the sulfide be added rapidly the fugitive appearance of colloidal sulfur can be observed but it immediately dissolves. We, therefore, became interested to know if the same result would be obtained if the reaction was carried out in basic solution in the presence of an excess of hypochlorite and then acidified. This was found to be the case except that the resolution of the sulfur was not instantaneous but required
from one to several minutes depending upon the time the basic solution was allowed to stand before addition of the acid (coagulation effect). The results of a typical run are shown in Table 27, where the approximate rate of conversion with time has been determined.

2. Temperature Effect

The reaction was studied at the following temperatures:

- $0^\circ$ C.
- $25^\circ$
- $50^\circ$
- $75^\circ$
- $100^\circ$

The reaction was studied at $0^\circ$ by allowing portions of sulfide and hypochlorite to come to $0^\circ$ in an ice bath and then mixing. The ratio of hypochlorite to sulfide was then determined in the manner previously discussed.

The reaction was run at $25^\circ$, $50^\circ$, and $75^\circ$ in a thermostat accurate to $\pm 1^\circ$ which proved to be accurate enough since at the lower temperatures the temperature effect is relatively small and at the higher temperatures there are several sources of error which are larger than any error produced by a variation of a degree or so in temperature.

The reaction at $100^\circ$ was run by bringing the reactants to a boil and mixing. This temperature will be a fraction of a degree higher than $100^\circ$ due to the presence of electrolytes but this error is negligibly small.

The results of the investigation of the effect of
temperature are given in Tables 28, 29, 30, 31, and 32.

It is evident that high temperatures favor the formation of sulfate and low temperatures favor the formation of sulfur. Also, at temperatures up to 50° the ratio remains practically constant for various quantities of sulfide added to a constant volume of hypochlorite, but above this temperature there is a considerable variation.

Although sodium hypochlorite solutions are comparatively stable at ordinary temperatures, they rapidly decompose at higher temperatures yielding chlorate so at the higher temperatures and particularly at 100° we are probably studying the action of chlorate rather than hypochlorite on sulfide.

There are other factors also which become prominent at the higher temperatures such as the rapid action of base on sulfur as well as the rapid oxidation of sulfide by atmospheric oxidation.

It is evident, therefore, that we cannot lay much emphasis on the results at 75° and 100° but they were determined more or less for the sake of information and also to better round out the study of the effect of temperature.

The effect of temperature at 0°, 25°, and 50° is probably the true effect of temperature on the mechanism, since the secondary reactions discussed above are negligible at these temperatures.
3. pH Effect

Throughout the foregoing study the author had realized that some other factor was acting other than concentration or temperature, and had concluded that it must be a pH effect. Stevens (8) had definitely shown that the reaction in acid and in basic solution was different. It became apparent, therefore, that for a complete understanding of the reaction, we would have to determine the course of the reaction at various pH values and we desired to do this over the entire pH scale if possible.

Since the reactants are both basic in nature and since base has been shown to be produced in the reaction, it was decided to control the pH by use of buffers. Those given by Clark and Lubs (409) were used in this work. In general the pH of the hypochlorite solutions will run slightly less than pH = 12 and the sulfide solutions slightly higher than 12 depending upon the concentration.

In this work it was found necessary to use rather dilute solutions since hypochlorite in acid solutions tends to lose chlorine. It was found convenient to use 100 cc. of buffer solution to which was added 10 cc. of the hypochlorite solution, and to this add quantities of sodium sulfide solution varying from 2 to 5 cc. The effect of dilution must be kept in mind, but by running as above there is at all times a hypochlorite solution of constant concentration. The concentration of the added sulfide is also
constant, and it was found that the slight variation of the quantity of sulfide solution added had no material effect. Thus, we should be measuring the effect of pH alone.

It was found that the pH of the buffer solution held very well upon the addition of 10 cc. of hypochlorite to 100 cc. of the buffer solution, although there was a few tenths of a pH change in practically all cases. It was further found that the addition of the sulfide solution caused no further change in the pH exceeding 0.1 pH in any case, so the pH of the solution of the buffer plus the hypochlorite was taken as the pH at which the reaction occurred.

All measurements of pH were made with a glass electrode and the potentiometric circuit as previously described.

The results are given in detail in Table 33, and summed up in Table 34. In the graph pH is plotted against the ratio of hypochlorite to sulfide.

From the graph it is seen that the curve is comparatively smooth with a distinct minimum at about a pH of 10, the ratio increasing both to the left and to the right of this critical value. Towards the acid end there is a gradual increase in the formation of sulfate from pH of 10 to pH of 2 where there is a quantitative formation of sulfate. On the basic side of pH 10 there is a more rapid rise in the curve which also indicates increase of sulfate. It is evident that as we increase the concentration of base we approach a ratio of 4 and if the basicity of the reaction
medium is increased to 3 N, no sulfur appears in the reaction and the ratio becomes 3.98 or 4 within experimental error. This indicates that in basic solutions, 4 is again the limiting value, i.e. quantitative conversion to sulfate.

Since it is known that thiosulfate is one of the products of the reaction of sodium hydroxide on sulfur, we wished to know the action of sodium hypochlorite on thiosulfate at a pH of 14 (1.5 N with NaOH). The results are shown in Table 35. The ratio of thiosulfate to hypochlorite is seen to be 6.04. The theoretical ratio of hypochlorite to thiosulfate for the quantitative oxidation of thiosulfate to sulfate is 8.00. It is evident, therefore, that there is a quantitative conversion of thiosulfate to sulfate by an excess of hypochlorite at this concentration of base.
DATA
TABLE 1
PRELIMINARY INVESTIGATION

QUALITATIVE TESTS FOR SULFIDE AND SULFATE UPON THE ADDITION OF INCREASING QUANTITIES OF SULFIDE TO A GIVEN AMOUNT OF HYPOCHLORITE. DETERMINATION OF RESIDUAL OXIDIZING OR REDUCING POWER, DETERMINATION OF CHANGE IN BASICITY

Solutions: 0.004740 N Na$_2$S
0.005000 N NaOCl
0.005000 N HCl
0.01000 N Na$_2$S$_2$O$_3$

NaOCl constant at 50 cc.

<table>
<thead>
<tr>
<th>cc. Na$_2$S</th>
<th>Ox. Power</th>
<th>Basicity HCl</th>
<th>Test Sulfide</th>
<th>Test Sulfate</th>
<th>Red. Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>20.25</td>
<td>39.91</td>
<td>Neg.</td>
<td>Pos.</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>16.27</td>
<td>42.50</td>
<td>#</td>
<td>#</td>
<td>--</td>
</tr>
<tr>
<td>15</td>
<td>11.58</td>
<td>44.00</td>
<td>#</td>
<td>#</td>
<td>--</td>
</tr>
<tr>
<td>20</td>
<td>7.71</td>
<td>45.94</td>
<td>#</td>
<td>#</td>
<td>--</td>
</tr>
<tr>
<td>25</td>
<td>3.35</td>
<td>47.80</td>
<td>#</td>
<td>#</td>
<td>--</td>
</tr>
<tr>
<td>30</td>
<td>--</td>
<td>49.73</td>
<td>Pos.</td>
<td>#</td>
<td>0.30</td>
</tr>
<tr>
<td>35</td>
<td>--</td>
<td>51.47</td>
<td>#</td>
<td>#</td>
<td>2.30</td>
</tr>
<tr>
<td>40</td>
<td>--</td>
<td>53.15</td>
<td>#</td>
<td>#</td>
<td>4.30</td>
</tr>
<tr>
<td>45</td>
<td>--</td>
<td>55.12</td>
<td>#</td>
<td>#</td>
<td>6.28</td>
</tr>
<tr>
<td>50</td>
<td>--</td>
<td>56.18</td>
<td>#</td>
<td>#</td>
<td>7.87</td>
</tr>
</tbody>
</table>

NOTE: Original basicity/50 cc. NaOCl = 38.19 cc. HCl

* * /25 cc. Na$_2$S = 8.66 * *
TABLE 2

DETERMINATION OF THE RATIO OF EQUIVALENTS OF NaOCl TO EQUIVALENTS OF Na₂S USED IN THE REACTION FROM THE DATA IN TABLE 1

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl x 10⁴</th>
<th>Eq. Na₂S x 10⁴</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>20.23</td>
<td>4.77</td>
<td>2.37</td>
<td>2.01</td>
</tr>
<tr>
<td>10.00</td>
<td>16.27</td>
<td>8.75</td>
<td>4.74</td>
<td>1.84</td>
</tr>
<tr>
<td>15.00</td>
<td>11.23</td>
<td>13.12</td>
<td>7.11</td>
<td>1.85</td>
</tr>
<tr>
<td>20.00</td>
<td>7.71</td>
<td>17.29</td>
<td>9.43</td>
<td>1.82</td>
</tr>
<tr>
<td>25.00</td>
<td>3.35</td>
<td>21.65</td>
<td>11.85</td>
<td>1.83</td>
</tr>
</tbody>
</table>

| 1.84 |

TABLE 3

DETERMINATION OF THE RATIO NaOCl/Na₂S IN APPROXIMATELY 0.2 N SOLUTIONS

Temp. = 25°

Solutions:
- 0.2321 N Na₂S
- 0.2256 N NaOCl
- 0.1068 N I
- 0.1038 N Na₂S₂O₃

NaOCl constant at 25 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl x 10⁴</th>
<th>Eq. Na₂S x 10⁴</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>43.70</td>
<td>1.11</td>
<td>0.58</td>
<td>1.91</td>
</tr>
<tr>
<td>5.00</td>
<td>33.50</td>
<td>2.16</td>
<td>1.16</td>
<td>1.86</td>
</tr>
<tr>
<td>7.50</td>
<td>23.20</td>
<td>3.22</td>
<td>1.74</td>
<td>1.85</td>
</tr>
<tr>
<td>10.00</td>
<td>13.95</td>
<td>4.19</td>
<td>2.32</td>
<td>1.81</td>
</tr>
<tr>
<td>12.50</td>
<td>2.12</td>
<td>5.41</td>
<td>2.90</td>
<td>1.86</td>
</tr>
</tbody>
</table>

1.86
TABLE 4

DETERMINATION OF THE RATIO NaOCl/NaS IN APPROXIMATELY 0.1 N SOLUTIONS

Solutions: 0.1200 N NaS  Temp. = 25°
0.1050 N NaOCl
0.1063 N I
0.1088 N Na₂S₂O₃

NaOCl constant at 50 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl x 10³</th>
<th>Eq. Na₂S x 10³</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>40.21</td>
<td>1.065</td>
<td>0.800</td>
<td>1.73</td>
</tr>
<tr>
<td>10.00</td>
<td>30.14</td>
<td>2.120</td>
<td>1.200</td>
<td>1.77</td>
</tr>
<tr>
<td>15.00</td>
<td>19.92</td>
<td>3.180</td>
<td>1.800</td>
<td>1.77</td>
</tr>
<tr>
<td>20.00</td>
<td>8.65</td>
<td>4.350</td>
<td>2.400</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.78</td>
</tr>
</tbody>
</table>

TABLE 5

DETERMINATION OF THE RATIO NaOCl/NaS IN APPROXIMATELY 0.05 N SOLUTIONS

Solutions: 0.0515 N NaOCl  Temp. = 25°
0.0561 N Na₂S
0.1062 N I
0.1033 N Na₂S₂O₃

NaOCl constant at 50 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl x 10³</th>
<th>Eq. Na₂S x 10³</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>19.70</td>
<td>0.545</td>
<td>0.2305</td>
<td>1.94</td>
</tr>
<tr>
<td>10.00</td>
<td>14.80</td>
<td>1.050</td>
<td>0.5610</td>
<td>1.87</td>
</tr>
<tr>
<td>15.00</td>
<td>10.00</td>
<td>1.549</td>
<td>0.8415</td>
<td>1.84</td>
</tr>
<tr>
<td>20.00</td>
<td>4.55</td>
<td>2.110</td>
<td>1.122</td>
<td>1.88</td>
</tr>
<tr>
<td>25.00</td>
<td>0.43</td>
<td>2.540</td>
<td>1.349</td>
<td>1.88</td>
</tr>
</tbody>
</table>
TABLE 6

INVESTIGATION OF THE APPLICABILITY OF THE BENZIDINE SULFATE
METHOD TO THE DETERMINATION OF THE QUANTITY OF SULFATE
ARISING IN THE REACTION BETWEEN NAOCL AND NA₂S AT
AT CONCENTRATIONS OF APPROXIMATELY 0.2 N

Solutions: Known sulfate solution
(2.6428 gm. (NH₄)₂SO₄/L)
Benzidine hydrochloride solution
0.05467 N NaOH

<table>
<thead>
<tr>
<th>Known Eq. S₀₄</th>
<th>cc. NaOH</th>
<th>Expt'l Eq. S₀₄</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0002</td>
<td>2.74</td>
<td>0.0002045</td>
<td>+2.25</td>
</tr>
<tr>
<td>0.0004</td>
<td>7.20</td>
<td>0.0003936</td>
<td>-1.60</td>
</tr>
<tr>
<td>0.0006</td>
<td>11.00</td>
<td>0.0006014</td>
<td>+0.23</td>
</tr>
<tr>
<td>0.0008</td>
<td>14.70</td>
<td>0.0008037</td>
<td>+0.50</td>
</tr>
<tr>
<td>0.0010</td>
<td>18.00</td>
<td>0.0009841</td>
<td>-1.59</td>
</tr>
</tbody>
</table>

TABLE 7

APPLICATION OF THE METHOD TO THE DETERMINATION OF SULFATE
PRODUCED IN THE REACTION BETWEEN SULFIDE AND HYPOCHLORITE
METHOD 1

Solutions: 0.2125 N NaOCl  Temp. = 24°
0.2125 N Na₂S
0.05467 N NaOH
Benzidine hydrochloride

NaOCl constant at 50.00 cc.

<table>
<thead>
<tr>
<th>Na₂S cc.</th>
<th>NaOH cc.</th>
<th>Eq. S₀₄ x 10³</th>
<th>Eq. Sulfide x 10³</th>
<th>Eq. S x 10³</th>
<th>Ratio S/S₀₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>5.40</td>
<td>0.2954</td>
<td>1.0625</td>
<td>0.7671</td>
<td>2.60</td>
</tr>
<tr>
<td>10.00</td>
<td>17.37</td>
<td>0.9501</td>
<td>2.1250</td>
<td>1.1749</td>
<td>1.34</td>
</tr>
<tr>
<td>15.00</td>
<td>22.50</td>
<td>1.221</td>
<td>3.1875</td>
<td>1.9585</td>
<td>1.59</td>
</tr>
<tr>
<td>20.00</td>
<td>27.90</td>
<td>1.526</td>
<td>4.2500</td>
<td>2.7240</td>
<td>1.79</td>
</tr>
<tr>
<td>25.00</td>
<td>33.70</td>
<td>1.843</td>
<td>5.3125</td>
<td>3.4695</td>
<td>1.88</td>
</tr>
<tr>
<td>$\text{Na}_2\text{S}$</td>
<td>$\text{NaOH}$</td>
<td>Eq. $\text{SO}_4$ $\times 10^3$</td>
<td>Eq. Sulfide $\times 10^3$</td>
<td>Eq. S $\times 10^3$</td>
<td>Ratio $\text{S}/\text{SO}_4$</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5.00</td>
<td>6.99</td>
<td>0.3321</td>
<td>1.11</td>
<td>0.728</td>
<td>1.50</td>
</tr>
<tr>
<td>10.00</td>
<td>14.70</td>
<td>0.8037</td>
<td>2.22</td>
<td>1.416</td>
<td>1.77</td>
</tr>
<tr>
<td>15.00</td>
<td>23.27</td>
<td>1.272</td>
<td>3.33</td>
<td>2.06</td>
<td>1.62</td>
</tr>
<tr>
<td>20.00</td>
<td>31.55</td>
<td>1.725</td>
<td>4.44</td>
<td>2.72</td>
<td>1.58</td>
</tr>
<tr>
<td>25.00</td>
<td>41.00</td>
<td>2.241</td>
<td>5.55</td>
<td>3.31</td>
<td>1.48</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\text{Na}_2\text{S}$</th>
<th>$\text{NaOH}$</th>
<th>Eq. $\text{SO}_4$ $\times 10^3$</th>
<th>Eq. Sulfide $\times 10^3$</th>
<th>Eq. S $\times 10^3$</th>
<th>Ratio $\text{S}/\text{SO}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>8.01</td>
<td>0.4379</td>
<td>0.076</td>
<td>0.638</td>
<td>1.45</td>
</tr>
<tr>
<td>10.00</td>
<td>20.03</td>
<td>1.085</td>
<td>2.152</td>
<td>1.057</td>
<td>0.985</td>
</tr>
<tr>
<td>15.00</td>
<td>27.25</td>
<td>1.430</td>
<td>3.228</td>
<td>1.738</td>
<td>1.165</td>
</tr>
<tr>
<td>20.00</td>
<td>31.60</td>
<td>1.728</td>
<td>4.304</td>
<td>2.576</td>
<td>1.49</td>
</tr>
<tr>
<td>25.00</td>
<td>36.25</td>
<td>1.982</td>
<td>5.380</td>
<td>3.398</td>
<td>1.71</td>
</tr>
</tbody>
</table>
### TABLE 10
**DETERMINATION OF SULFATE METHOD 4**

Solutions: 0.2870 N Na₂S  
0.2400 N NaOCl  
0.05467 N NaOH  
Benzidine hydrochloride

25 cc. NaOCl + 10 cc. Na₂S + 50 cc. 0.1 N acid + 20 cc. H₂O₂

<table>
<thead>
<tr>
<th>Soln. No.</th>
<th>NaOH cc.</th>
<th>Eq. SO₄ x 10⁻³</th>
<th>Eq. Na₂S x 10⁻³</th>
<th>Eq. S x 10⁻³</th>
<th>Ratio S/SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.74</td>
<td>0.697</td>
<td>2.27</td>
<td>1.575</td>
<td>2.26</td>
</tr>
<tr>
<td>2</td>
<td>12.83</td>
<td>0.703</td>
<td>1.587</td>
<td>2.23</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>12.51</td>
<td>0.684</td>
<td>1.586</td>
<td>2.32</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>12.79</td>
<td>0.693</td>
<td>1.572</td>
<td>2.26</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 11
**DETERMINATION OF THE SULFATE CONTENT OF 3% HYDROGEN PEROXIDE BY THE BENZIDINE SULFATE METHOD**

Solutions: 0.05467 N NaOH  
Benzidine hydrochloride

<table>
<thead>
<tr>
<th>cc. H₂O₂</th>
<th>cc. NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.00</td>
<td>0.67</td>
</tr>
<tr>
<td>20.00</td>
<td>0.68</td>
</tr>
</tbody>
</table>

### TABLE 12
**CORRECTION OF TABLE 10 FOR SULFATE IN HYDROGEN PEROXIDE**

<table>
<thead>
<tr>
<th>Soln. No.</th>
<th>Ratio S/SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.44</td>
</tr>
<tr>
<td>2</td>
<td>2.42</td>
</tr>
<tr>
<td>3</td>
<td>2.50</td>
</tr>
<tr>
<td>4</td>
<td>2.44</td>
</tr>
</tbody>
</table>
TABLE 13

DETERMINATION OF THE SULFATE CONTENT OF 30% HYDROGEN PEROXIDE

Solutions: 0.05467 N NaOH
Benzidine hydrochloride

<table>
<thead>
<tr>
<th>cc. H₂O₂</th>
<th>cc. NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>1.61</td>
</tr>
<tr>
<td>10.00</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>1.65</td>
</tr>
</tbody>
</table>

TABLE 14

DETERMINATION OF SULFATE FORMED IN THE REACTION BETWEEN NaOCl AND Na₂S OF APPROXIMATELY 0.2 N

Solutions: 0.222 N Na₂S  Temp. = 24°C
0.240 N NaOCl
0.05467 N NaOH
Benzidine hydrochloride

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. NaOH Corrected</th>
<th>Eq. S0₄ x 10³</th>
<th>Eq. S x 10³</th>
<th>Eq. S x 10⁵</th>
<th>Ratio S/SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>10.32</td>
<td>0.655</td>
<td>2.22</td>
<td>1.565</td>
<td>2.40</td>
</tr>
<tr>
<td>15.00</td>
<td>17.19</td>
<td>0.941</td>
<td>3.33</td>
<td>2.389</td>
<td>2.52</td>
</tr>
<tr>
<td>20.00</td>
<td>24.88</td>
<td>1.360</td>
<td>4.44</td>
<td>3.080</td>
<td>2.26</td>
</tr>
<tr>
<td>25.00</td>
<td>30.35</td>
<td>1.660</td>
<td>5.55</td>
<td>3.390</td>
<td>2.40</td>
</tr>
</tbody>
</table>
**TABLE 15**

**INVESTIGATION OF THE EFFECT OF INCREASING SULFIDE CONCENTRATION OVER THAT OF HYPOCHLORITE**

Solutions: 0.00545 N NaOCl  
Temp. = 24°  
Na₂S as shown  
0.01115 N Na₂S₂O₃

NaOCl constant at 100 cc.

<table>
<thead>
<tr>
<th>Conc. Na₂S</th>
<th>Na₂S</th>
<th>Eq. Na₂S</th>
<th>Na₂S₂O₃</th>
<th>Eq. NaOCl</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2290</td>
<td>1.00</td>
<td>229</td>
<td>15.88</td>
<td>366</td>
<td>1.60</td>
</tr>
<tr>
<td>1.20</td>
<td></td>
<td>271</td>
<td>11.40</td>
<td>436</td>
<td>1.64</td>
</tr>
<tr>
<td>0.1610</td>
<td>1.50</td>
<td>242</td>
<td>12.67</td>
<td>404</td>
<td>1.67</td>
</tr>
<tr>
<td>1.50</td>
<td></td>
<td>242</td>
<td>12.44</td>
<td>406</td>
<td>1.68</td>
</tr>
<tr>
<td>0.1035</td>
<td>2.00</td>
<td>207</td>
<td>13.66</td>
<td>337</td>
<td>1.62</td>
</tr>
<tr>
<td>2.00</td>
<td></td>
<td>207</td>
<td>13.11</td>
<td>332</td>
<td>1.60</td>
</tr>
<tr>
<td>0.0710</td>
<td>3.00</td>
<td>213</td>
<td>16.68</td>
<td>359</td>
<td>1.69</td>
</tr>
<tr>
<td>4.00</td>
<td></td>
<td>284</td>
<td>5.66</td>
<td>480</td>
<td>1.69</td>
</tr>
<tr>
<td>0.0497</td>
<td>5.00</td>
<td>248.5</td>
<td>9.75</td>
<td>436</td>
<td>1.75</td>
</tr>
<tr>
<td>0.0498</td>
<td>5.00</td>
<td>246.5</td>
<td>9.88</td>
<td>435</td>
<td>1.76</td>
</tr>
<tr>
<td>0.00474</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.84</td>
</tr>
</tbody>
</table>

**TABLE 16**

**DETERMINATION OF THE EFFECT OF THE RATE OF ADDITION OF Na₂S TO NaOCl**

Solutions: 0.00545 N NaOCl  
Temp. = 24°

0.04923 N Na₂S  
0.01115 N Na₂S₂O₃

<table>
<thead>
<tr>
<th>Rate</th>
<th>Eq. Na₂S x 10⁶</th>
<th>Eq. NaOCl x 10⁶</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAST</td>
<td>246.5</td>
<td>441.5</td>
<td>1.67</td>
</tr>
<tr>
<td>10-15 Sec.</td>
<td>246.5</td>
<td>414.5</td>
<td>1.69</td>
</tr>
<tr>
<td>SLOW</td>
<td>246.5</td>
<td>435.0</td>
<td>1.76</td>
</tr>
<tr>
<td>200 Sec.</td>
<td>246.5</td>
<td>426.2</td>
<td>1.75</td>
</tr>
</tbody>
</table>
### TABLE 17

**DETERMINATION OF THE EFFECT OF ADDING NaOCl TO Na₂S**

Solutions: 0.00545 N NaOCl  \[\text{Temp. } = 24^\circ\]
0.04930 N Na₂S
0.01115 N Na₂S₂O₃

Add 100 cc. NaOCl to 5 cc. Na₂S

<table>
<thead>
<tr>
<th>Eq. Na₂S x 10⁶</th>
<th>Eq. NaOCl x 10⁶</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>246.5</td>
<td>401.5</td>
<td>1.63</td>
</tr>
<tr>
<td>246.5</td>
<td>394.0</td>
<td>1.60</td>
</tr>
</tbody>
</table>

### TABLE 18

**DETERMINATION OF THE RATIO WHEN VARIOUS QUANTITIES OF APPROXIMATELY 0.05 SULFIDE ARE ADDED TO A DEFINITE AMOUNT OF APPROXIMATELY 0.3 N HYPOCHLORITE**

Solutions: 0.0477 N Na₂S  \[\text{Temp. } = 25^\circ\]
0.3050 N NaOCl
0.1001 N Na₂S₂O₃

NaOCl constant at 10.00 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. Na₂S x 10⁶</th>
<th>Eq. NaOCl x 10⁶</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>24.76</td>
<td>238.5</td>
<td>574</td>
<td>2.40</td>
</tr>
<tr>
<td>10.00</td>
<td>19.35</td>
<td>477</td>
<td>1115</td>
<td>2.34</td>
</tr>
<tr>
<td>15.00</td>
<td>14.42</td>
<td>715</td>
<td>1608</td>
<td>2.25</td>
</tr>
<tr>
<td>20.00</td>
<td>9.62</td>
<td>954</td>
<td>2088</td>
<td>2.19</td>
</tr>
<tr>
<td>25.00</td>
<td>4.47</td>
<td>1191</td>
<td>2603</td>
<td>2.13</td>
</tr>
<tr>
<td>30.00</td>
<td>0.13</td>
<td>1431</td>
<td>3037</td>
<td>2.12</td>
</tr>
</tbody>
</table>
TABLE 19

DETERMINATION OF THE EFFECT OF INCREASING HYPOCHLORITE CONCENTRATION OVER THAT OF SULFIDE

Solutions: 0.0203 N Na₂S  
NaOCl as shown  
0.1001 N Na₂S₂O₃  
Temp. = 23°

<table>
<thead>
<tr>
<th>Conc. NaOCl</th>
<th>Eq. Na₂S x 10⁶</th>
<th>Eq. NaOCl x 10⁶</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3050</td>
<td>203</td>
<td>602</td>
<td>2.96</td>
</tr>
<tr>
<td>0.2024</td>
<td>203</td>
<td>527</td>
<td>2.64</td>
</tr>
<tr>
<td>0.1503</td>
<td>203</td>
<td>469</td>
<td>2.31</td>
</tr>
<tr>
<td>0.0980</td>
<td>203</td>
<td>440</td>
<td>2.14</td>
</tr>
<tr>
<td>0.0525</td>
<td>304.5</td>
<td>628</td>
<td>2.06</td>
</tr>
<tr>
<td>0.0185</td>
<td>182.7</td>
<td>340</td>
<td>1.86</td>
</tr>
</tbody>
</table>

TABLE 20

DETERMINATION OF THE RATE OF REACTION OF NAOCL ON COLLOIDAL SULFUR IN BASIC SOLUTION

Solutions: 0.0523 N Na₂S  
0.1032 N NaOCl  
0.1001 N Na₂S₂O₃  
Basicity about 0.1 N  
0.1061 N I  
Temp. = 24°

15 cc. Na₂S added to 25 cc. NaOCl and the residual oxidizing power determined on separate solutions at the time intervals shown.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>cc. Na₂S₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.81</td>
</tr>
<tr>
<td>5</td>
<td>10.81</td>
</tr>
<tr>
<td>20</td>
<td>10.43</td>
</tr>
<tr>
<td>37</td>
<td>10.41</td>
</tr>
<tr>
<td>98</td>
<td>9.97</td>
</tr>
</tbody>
</table>
### TABLE 21
STUDY OF THE RATE OF REACTION OF NaOH ON COLLOIDAL SULFUR
BASIC NORMALITY = 0.0808

<table>
<thead>
<tr>
<th>Time</th>
<th>cc. Na$_2$S$_2$O$_3$</th>
<th>Eq. cc. I</th>
<th>cc. I Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>17 min.</td>
<td>18.70</td>
<td>19.90</td>
<td>5.10</td>
</tr>
<tr>
<td>34</td>
<td>18.15</td>
<td>19.30</td>
<td>5.70</td>
</tr>
<tr>
<td>59</td>
<td>14.80</td>
<td>15.20</td>
<td>9.30</td>
</tr>
<tr>
<td>16.3 hrs.</td>
<td>13.02</td>
<td>12.84</td>
<td>11.16</td>
</tr>
</tbody>
</table>

### TABLE 22
STUDY OF THE RATE OF REACTION OF NaOH ON COLLOIDAL SULFUR
BASIC NORMALITY = 1.0

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>cc. Na$_2$S$_2$O$_3$</th>
<th>Eq. cc. I</th>
<th>cc. I Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18.70</td>
<td>19.90</td>
<td>5.10</td>
</tr>
<tr>
<td>14</td>
<td>18.15</td>
<td>19.30</td>
<td>5.70</td>
</tr>
<tr>
<td>41</td>
<td>14.80</td>
<td>15.20</td>
<td>9.30</td>
</tr>
<tr>
<td>253</td>
<td>13.02</td>
<td>12.84</td>
<td>11.16</td>
</tr>
</tbody>
</table>
### Table 23

**Study of the Rate of Reaction of NaOH on Colloidal Sulfur**

Base Normality = 2.0

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>cc. Na$_2$S$_2$O$_3$</th>
<th>Eq. cc. I</th>
<th>cc. I Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>18.55</td>
<td>19.82</td>
<td>5.18</td>
</tr>
<tr>
<td>30</td>
<td>18.48</td>
<td>19.64</td>
<td>5.36</td>
</tr>
<tr>
<td>45</td>
<td>17.95</td>
<td>18.99</td>
<td>6.01</td>
</tr>
<tr>
<td>60</td>
<td>17.80</td>
<td>18.40</td>
<td>6.60</td>
</tr>
<tr>
<td>75</td>
<td>17.14</td>
<td>18.23</td>
<td>6.77</td>
</tr>
<tr>
<td>90</td>
<td>16.61</td>
<td>17.70</td>
<td>7.30</td>
</tr>
<tr>
<td>105</td>
<td>16.10</td>
<td>17.10</td>
<td>7.90</td>
</tr>
<tr>
<td>120</td>
<td>15.32</td>
<td>16.30</td>
<td>8.70</td>
</tr>
</tbody>
</table>

### Table 24

**Study of the Rate of Reaction of NaOH on Colloidal Sulfur**

Base Normality = 2.0

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>cc. Na$_2$S$_2$O$_3$</th>
<th>Eq. cc. I</th>
<th>cc. I Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>4.40</td>
<td>4.17</td>
<td>5.63</td>
</tr>
<tr>
<td>30</td>
<td>4.08</td>
<td>3.86</td>
<td>6.14</td>
</tr>
<tr>
<td>45</td>
<td>3.92</td>
<td>3.71</td>
<td>6.29</td>
</tr>
<tr>
<td>60</td>
<td>3.51</td>
<td>3.32</td>
<td>6.63</td>
</tr>
<tr>
<td>105</td>
<td>2.96</td>
<td>2.80</td>
<td>7.20</td>
</tr>
<tr>
<td>cc. Na$_2$S</td>
<td>cc. Na$_2$S$_2$O$_3$</td>
<td>Eq. NaOCl x 10$^3$</td>
<td>Eq. Na$_2$S x 10$^3$</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>4.00</td>
<td>29.52</td>
<td>2.160</td>
<td>0.448</td>
</tr>
<tr>
<td>5.00</td>
<td>23.70</td>
<td>2.245</td>
<td>0.580</td>
</tr>
<tr>
<td>7.50</td>
<td>17.92</td>
<td>3.360</td>
<td>0.840</td>
</tr>
<tr>
<td>10.00</td>
<td>7.20</td>
<td>4.460</td>
<td>1.120</td>
</tr>
<tr>
<td>11.00</td>
<td>2.56</td>
<td>4.950</td>
<td>1.250</td>
</tr>
</tbody>
</table>

(x)This solution acidified without dilution. High value due to loss of chlorine. Not included in average.
**TABLE 26**

DETERMINATION OF THE RATIO NaOCl/Na₂S IN ACID SOLUTION WITH APPROXIMATELY 0.05 M SOLUTIONS - PH ABOUT 1

Solutions: 0.0561 N Na₂S  
0.0515 N NaOCl  
0.1062 N I  
0.1033 N Na₂S₂O₃  

Temp. = 22°

NaOCl constant at 50 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl $\times 10^3$</th>
<th>Eq. Na₂S $\times 10^3$</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>18.20</td>
<td>0.700</td>
<td>0.1683</td>
<td>4.15(x)</td>
</tr>
<tr>
<td>5.00</td>
<td>13.70</td>
<td>1.163</td>
<td>0.2305</td>
<td>4.00</td>
</tr>
<tr>
<td>7.00</td>
<td>9.65</td>
<td>1.586</td>
<td>0.3927</td>
<td>4.04</td>
</tr>
<tr>
<td>9.00</td>
<td>5.33</td>
<td>2.030</td>
<td>0.5049</td>
<td>4.02</td>
</tr>
<tr>
<td>10.50</td>
<td>2.34</td>
<td>2.340</td>
<td>0.5900</td>
<td>3.97</td>
</tr>
</tbody>
</table>

(x) Not included in average.
### TABLE 27

**STUDY OF THE EFFECT OF ADDITION OF ACID AFTER THE ADDITION OF SULFIDE**

<table>
<thead>
<tr>
<th>Time</th>
<th>Na$_2$S$_2$O$_3$ cc.</th>
<th>Eq. NaOCl x 10$^3$</th>
<th>Eq. Na$_2$S x 10$^3$</th>
<th>Ratio NaOCl/Na$_2$S</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 sec.</td>
<td>15.00</td>
<td>1.030</td>
<td>0.3927</td>
<td>2.62</td>
<td>65</td>
</tr>
<tr>
<td>15 sec.</td>
<td>11.68</td>
<td>1.37</td>
<td>0.3927</td>
<td>3.48</td>
<td>87</td>
</tr>
<tr>
<td>3 min.</td>
<td>9.92</td>
<td>1.557</td>
<td>0.3927</td>
<td>3.96</td>
<td>99</td>
</tr>
</tbody>
</table>

### TABLE 28

**DETERMINATION OF THE RATIO NaOCl/Na$_2$S AT 0$^o$ C.**

<table>
<thead>
<tr>
<th>cc. Na$_2$S</th>
<th>cc. Na$_2$S$_2$O$_3$</th>
<th>Eq. NaOCl x 10$^3$</th>
<th>Eq. Na$_2$S x 10$^3$</th>
<th>Ratio NaOCl/Na$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>20.00</td>
<td>0.485</td>
<td>0.272</td>
<td>1.71</td>
</tr>
<tr>
<td>10.00</td>
<td>14.60</td>
<td>0.940</td>
<td>0.544</td>
<td>1.73</td>
</tr>
<tr>
<td>15.00</td>
<td>10.83</td>
<td>1.411</td>
<td>0.816</td>
<td>1.74</td>
</tr>
<tr>
<td>20.00</td>
<td>8.20</td>
<td>1.890</td>
<td>1.088</td>
<td>1.70</td>
</tr>
<tr>
<td>25.00</td>
<td>2.15</td>
<td>2.310</td>
<td>1.360</td>
<td>1.73</td>
</tr>
</tbody>
</table>

NaOCl constant at 50 cc.
Na$_2$S constant at 7.00 cc.
TABLE 29
DETERMINATION OF THE RATIO NAOCL/NA₂S AT 25° C.

Solutions: 0.0515 N NaOCl
0.0561 N Na₂S
0.1062 N I
0.1033 N Na₂S₂O₃

NaOCl constant at 50 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl x 10³</th>
<th>Eq. Na₂S x 10³</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>19.70</td>
<td>0.545</td>
<td>0.2805</td>
<td>1.94(x)</td>
</tr>
<tr>
<td>10.00</td>
<td>14.80</td>
<td>1.050</td>
<td>0.5610</td>
<td>1.97</td>
</tr>
<tr>
<td>15.00</td>
<td>10.00</td>
<td>1.549</td>
<td>0.8415</td>
<td>1.84</td>
</tr>
<tr>
<td>20.00</td>
<td>4.55</td>
<td>2.110</td>
<td>1.1220</td>
<td>1.88</td>
</tr>
<tr>
<td>25.00</td>
<td>0.43</td>
<td>2.540</td>
<td>1.3490</td>
<td>1.88</td>
</tr>
</tbody>
</table>

(x) Not included in average.

TABLE 30
DETERMINATION OF THE RATIO NAOCL/NA₂S AT 50° C.

Solutions: 0.0561 N Na₂S
0.0507 N NaOCl
0.1062 N I
0.1033 N Na₂S₂O₃

NaOCl constant at 50 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl x 10³</th>
<th>Eq. Na₂S x 10³</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>19.70</td>
<td>0.559</td>
<td>0.2805</td>
<td>2.02</td>
</tr>
<tr>
<td>10.00</td>
<td>13.70</td>
<td>1.117</td>
<td>0.5610</td>
<td>1.99</td>
</tr>
<tr>
<td>15.00</td>
<td>8.60</td>
<td>1.645</td>
<td>0.8415</td>
<td>1.96</td>
</tr>
<tr>
<td>20.00</td>
<td>3.15</td>
<td>2.205</td>
<td>1.1220</td>
<td>1.96</td>
</tr>
</tbody>
</table>
### TABLE 31

**DETERMINATION OF THE RATIO NaOCl/Na₂S AT 75°C.**

Solutions: 0.0560 N Na₂S  
0.0544 N NaOCl  
0.1062 N I  
0.1035 N Na₃S₂O₃

NaOCl constant at 50 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl x 10³</th>
<th>Eq. Na₂S x 10³</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.50</td>
<td>15.35</td>
<td>0.975</td>
<td>0.420</td>
<td>2.31</td>
</tr>
<tr>
<td>10.00</td>
<td>11.40</td>
<td>1.353</td>
<td>0.560</td>
<td>2.42</td>
</tr>
<tr>
<td>12.50</td>
<td>7.90</td>
<td>1.720</td>
<td>0.700</td>
<td>2.46</td>
</tr>
<tr>
<td>15.00</td>
<td>4.16</td>
<td>2.100</td>
<td>0.840</td>
<td>2.62</td>
</tr>
</tbody>
</table>

### TABLE 32

**DETERMINATION OF THE RATIO NaOCl/Na₂S AT 100°C.**

Solutions: 0.0560 N Na₂S  
0.0507 N NaOCl  
0.1062 N I  
0.1035 N Na₃S₂O₃

NaOCl constant at 50 cc.

<table>
<thead>
<tr>
<th>cc. Na₂S</th>
<th>cc. Na₂S₂O₃</th>
<th>Eq. NaOCl x 10³</th>
<th>Eq. Na₂S x 10³</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>14.56</td>
<td>1.027</td>
<td>0.280</td>
<td>3.66</td>
</tr>
<tr>
<td>5.00(x)</td>
<td>14.00</td>
<td>1.088</td>
<td>0.280</td>
<td>3.88</td>
</tr>
<tr>
<td>7.50</td>
<td>9.49</td>
<td>1.349</td>
<td>0.420</td>
<td>3.21</td>
</tr>
<tr>
<td>10.00</td>
<td>4.25</td>
<td>2.115</td>
<td>0.560</td>
<td>3.78</td>
</tr>
</tbody>
</table>

(x) Run from burette into boiling NaOCl. Others—both reactants brought to boil and mixed.
EFFECT OF TEMPERATURE ON THE RATIO NaOCl/Na₂S
TABLE 33

STUDY OF THE EFFECT OF PH ON THE RATIO NaOCl/Na$_2$S

**pH = 14**

Use 100 cc. of 3 N NaOH solution as the reaction medium.

This solution should approach a pH of 14.

Solutions: 0.06109 N Na$_2$S  
0.05045 N NaOCl  
0.1001 N Na$_2$S$_2$O$_3$

<table>
<thead>
<tr>
<th>Na$_2$S (cc.)</th>
<th>NaOCl (cc.)</th>
<th>Na$_2$S$_2$O$_3$ (cc.)</th>
<th>Eq. NaOCl $\times 10^6$</th>
<th>Eq. Na$_2$S $\times 10^6$</th>
<th>Ratio NaOCl/Na$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00</td>
<td>20.00</td>
<td>0.32(x)</td>
<td>969</td>
<td>244</td>
<td>3.98</td>
</tr>
</tbody>
</table>

(x) Corrected for blank which was 0.10 cc.

**pH = 14**

Use 100 cc. of 1.5 N NaOH solution as the reaction medium.

Solutions: 0.0523 N Na$_2$S  
0.0561 N NaOCl  
0.1001 N Na$_2$S$_2$O$_3$

<table>
<thead>
<tr>
<th>Na$_2$S (cc.)</th>
<th>NaOCl (cc.)</th>
<th>Na$_2$S$_2$O$_3$ (cc.)</th>
<th>Eq. NaOCl $\times 10^6$</th>
<th>Eq. Na$_2$S $\times 10^6$</th>
<th>Ratio NaOCl/Na$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.08</td>
<td>10.00</td>
<td>1.82</td>
<td>399</td>
<td>107.4</td>
<td>3.71</td>
</tr>
</tbody>
</table>

**pH = 13.4**

Use 100 cc. of 0.4 N NaOH as the reaction medium. This solution should give a pH of about 13.4

Solutions: 0.0511 N Na$_2$S  
0.0580 N NaOCl  
0.1001 N Na$_2$S$_2$O$_3$

<table>
<thead>
<tr>
<th>Na$_2$S (cc.)</th>
<th>NaOCl (cc.)</th>
<th>Na$_2$S$_2$O$_3$ (cc.)</th>
<th>Eq. NaOCl $\times 10^6$</th>
<th>Eq. Na$_2$S $\times 10^6$</th>
<th>Ratio NaOCl/Na$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>25.00</td>
<td>0.50</td>
<td>1400</td>
<td>511</td>
<td>2.74</td>
</tr>
</tbody>
</table>
Note: The actual pH values of the foregoing solutions could not be determined with the glass electrode since its range is limited on the basic side to a pH of 12.5. Accordingly, the foregoing values are estimated.

\[
\text{pH} = 11.8
\]

Use 100 cc. of distilled water as the reaction medium.

\[
\text{pH upon the addition of 10.00 cc. NaOCl} = 11.7
\]

\[
\text{pH upon the addition of 5.00 cc. Na}_2\text{S} = 11.8
\]

Solutions: 
0.0516 N Na\(_{2}\text{S}\)
0.0581 N NaOCl
0.1001 N Na\(_{2}\text{S}_2\text{O}_3\)

<table>
<thead>
<tr>
<th>Na(_{2}\text{S})</th>
<th>NaOCl</th>
<th>Na(_{2}\text{S}_2\text{O}_3)</th>
<th>Eq. NaOCl (x 10^6)</th>
<th>Eq. Na(_2\text{S}) (x 10^6)</th>
<th>Ratio NaOCl/Na(_2\text{S})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>10.00</td>
<td>1.50</td>
<td>450</td>
<td>258</td>
<td>1.67</td>
</tr>
</tbody>
</table>

\[
\text{pH} = 10.0
\]

Use as reaction medium 100 cc. of buffer solution prepared as follows:

43.90 cc. 0.1 N NaOH + 50 cc. 0.1 N H\(_2\text{BO}_3\) diluted to 100 cc.

\[
\text{pH of buffer} = 10.0
\]

plus 10 cc. NaOCl 10.0

Plus 5 cc. Na\(_2\text{S}\) 10.0

Solutions: 
0.0516 N Na\(_{2}\text{S}\)
0.0581 N NaOCl
0.1001 N Na\(_{2}\text{S}_2\text{O}_3\)

<table>
<thead>
<tr>
<th>Na(_{2}\text{S})</th>
<th>NaOCl</th>
<th>Na(_{2}\text{S}_2\text{O}_3)</th>
<th>Eq. NaOCl (x 10^6)</th>
<th>Eq. Na(_2\text{S}) (x 10^6)</th>
<th>Ratio NaOCl/Na(_2\text{S})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>10.00</td>
<td>1.95</td>
<td>386</td>
<td>258</td>
<td>1.50</td>
</tr>
</tbody>
</table>
pH = 8.4

Use as reaction medium 100 cc. of buffer solution prepared as follows:

3.97 cc. 0.1 N NaOH + 50 cc. 0.1 M H₂BO₃ diluted to 100 cc.

<table>
<thead>
<tr>
<th>pH of buffer</th>
<th>8.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>plus 10 cc. NaOCl</td>
<td>8.4</td>
</tr>
<tr>
<td>plus 5 cc. Na₂S</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Solutions: 0.0518 N Na₂S
0.0581 N NaOCl
0.1001 N Na₂SnO₃

<table>
<thead>
<tr>
<th>Na₂S</th>
<th>NaOCl</th>
<th>Na₂SnO₃</th>
<th>Eq. NaOCl</th>
<th>Eq. Na₂S</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>10.00</td>
<td>1.60</td>
<td>421</td>
<td>258</td>
<td>1.63</td>
</tr>
</tbody>
</table>

pH = 7.3

Use as reaction medium 100 cc. of buffer solution prepared as follows:

50 cc. 0.1 M KH₂PO₄ + 29.63 cc. 0.1 N NaOH diluted to 100 cc.

<table>
<thead>
<tr>
<th>pH of buffer</th>
<th>7.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>plus 10 cc. NaOCl</td>
<td>7.3</td>
</tr>
<tr>
<td>plus 4 cc. Na₂S</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Solutions: Same as above

<table>
<thead>
<tr>
<th>Na₂S</th>
<th>NaOCl</th>
<th>Na₂SnO₃</th>
<th>Eq. NaOCl</th>
<th>Eq. Na₂S</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.00</td>
<td>10.00</td>
<td>1.98</td>
<td>383</td>
<td>206.4</td>
<td>1.85</td>
</tr>
</tbody>
</table>
**pH = 5.4**

Use as reaction medium 100 cc. of buffer solution prepared as follows:

23.85 cc. 0.1 N NaOH + 50 cc. 0.1 M KHC₆H₄O₄ diluted to 100 cc.

- pH of buffer: 5.2
- plus 10 cc. NaOCl: 5.4
- plus 3 cc. Na₂S: 5.4

**Solutions: Same as foregoing**

<table>
<thead>
<tr>
<th>Na₂S (cc.)</th>
<th>NaOCl (cc.)</th>
<th>Na₂S₂O₃ (cc.)</th>
<th>Eq. NaOCl (x 10⁸)</th>
<th>Eq. Na₂S (x 10⁸)</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>10.00</td>
<td>1.18</td>
<td>463</td>
<td>154.8</td>
<td>3.00</td>
</tr>
</tbody>
</table>

**pH = 3.3**

Use as reaction medium 100 cc. of buffer solution prepared as follows:

20.32 cc. 0.1 N HCl + 50 cc. 0.1 M KHC₆H₄O₄ diluted to 100 cc.

- pH of buffer: 3.0
- plus 10 cc. NaOCl: 3.3
- plus 2 cc. Na₂S: 3.3

**Solutions: Same as foregoing**

<table>
<thead>
<tr>
<th>Na₂S (cc.)</th>
<th>NaOCl (cc.)</th>
<th>Na₂S₂O₃ (cc.)</th>
<th>Eq. NaOCl (x 10⁸)</th>
<th>Eq. Na₂S (x 10⁸)</th>
<th>Ratio NaOCl/Na₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>10.00</td>
<td>1.95</td>
<td>386</td>
<td>108.2</td>
<td>3.74</td>
</tr>
</tbody>
</table>
\[
\text{pH} = 2.0
\]

Use as reaction medium 100 cc. of buffer solution prepared as follows:

5.30 cc. 0.2 M HCl + 25 cc. 0.2 M KCl diluted to 100 cc.

\[
\begin{array}{cccc}
\text{pH of buffer} & \text{1.8} \\
\text{plus 10 cc. NaOCl} & \text{2.0} \\
\text{plus 2 cc. Na}_2\text{S} & \text{2.0} \\
\end{array}
\]

\[
\begin{array}{ccccccc}
\text{Na}_2\text{S} & \text{NaOCl} & \text{Na}_2\text{S}_2\text{O}_3 & \text{Eq. NaOCl} & \text{Eq. Na}_2\text{S} & \text{Ratio NaOCl/Na}_2\text{S} \\
\text{cc.} & \text{cc.} & \text{cc.} & \times 10^6 & \times 10^6 & \\
2.00 & 10.00 & 1.60 & 421 & 103.2 & 4.06(x) \\
\end{array}
\]

(x) This value ran higher than the theoretical 4.00 due to loss of chlorine.

\[
\text{pH} = 1.0 \text{ or lower}
\]

Acidities yielding pH values lower than 2 were found to give 4.00 for the ratio of NaOCl/Na\_2S.

See Tables 25, 26, and 27
### TABLE 34

**SUMMATION OF TABLE 33**

<table>
<thead>
<tr>
<th>pH</th>
<th>Ratio NaOCl/Na₅S</th>
<th>14.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.0</td>
<td>3.98</td>
<td></td>
</tr>
<tr>
<td>14.0⁻</td>
<td>3.71</td>
<td></td>
</tr>
<tr>
<td>13.4</td>
<td>2.74</td>
<td></td>
</tr>
<tr>
<td>11.8</td>
<td>1.87</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>8.4</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>7.3</td>
<td>1.85</td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>3.74</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>4.00</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 35

**DETERMINATION OF THE COURSE OF THE REACTION BETWEEN Na₅S₂O₅ AND NaOCl IN 1.5 N BASIC SOLUTION**

<table>
<thead>
<tr>
<th>Eq. NaOCl x 10⁴</th>
<th>Eq. Na₅S₂O₅ x 10⁴</th>
<th>Ratio NaOCl/Na₅S₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.04</td>
<td>1.00</td>
<td>8.04</td>
</tr>
</tbody>
</table>

Theoretical ratio for complete conversion of thiosulfate to sulfate equals 8.00
DISCUSSION OF RESULTS

Before proceeding with the explanation of the results and the evolution of a mechanism complying with the experimental findings it might be well to list the facts brought out in the foregoing sections:

At ordinary temperatures when the reactants are of approximately the same concentration, the ratio of NaOCl/Na₂S assumes a more or less constant value.

When the concentrations of the reactants are widely different, the ratio is found to change; high sulfide concentrations favoring the formation of sulfur, and high hypochlorite concentrations favoring the formation of sulfate.

The reaction has been shown to yield as final products sulfur and sulfate.

High temperatures favor the formation of sulfate.

The reaction has been shown to be quite markedly dependent on the pH of the reaction medium. A distinct minimum in the ratio NaOCl/Na₂S is found at a pH of about 10, the ratio increasing on both sides of this limiting value.

At pH values less than two there is a quantitative conversion of sulfide to sulfate by hypochlorite.

At a basicity of 3 N (pH = 14), no sulfur appears in the reaction and the ratio again assumed a value of 4 showing quantitative oxidation to sulfate.

If the reaction is run in basic solution and then acidified until the pH is 2 or less, the colloidal sulfur is rapidly and quantitatively converted to sulfate.

From the above summation it is evident that any proposed mechanism must answer the following questions:

Why does the ratio remain approximately constant when the reactants are of approximately the same concentration?
Why do high sulfide concentrations favor the formation of sulfur and high hypochlorite concentrations the formation of sulfate?

Why does the reaction ratio show a distinct minimum at a pH of 10 and why is there an increase in sulfate formation on each side of this critical value?

By what mechanism can we explain quantitative conversion to sulfate at pH values less than two and what difference is there in the mechanism which also gives quantitative conversion to sulfate at pH values of 14?

A study of the literature indicates that sulfur is probably the primary oxidation product of sulfides in all cases; however, this has not been definitely established in every case. A better realization of this mechanism is obtained with slow acting oxidants, e.g. the work of Bullock and Forbes (27). These investigators oxidized sulfide with certain aromatic nitro compounds and definitely proved that, although sulfur was not their end oxidation product, it was the primary oxidation product. They write their primary reaction as follows:

$$2Na_2S + RNO_2 + 4H_2O = 6NaOH + 3S + RNH_2$$

The formation of NaOH should be noted.

It has been shown (Table 1) that, in the oxidation of sulfide with hypochlorite, the appearance of sulfur is accompanied by an increase in basicity. Accordingly, the following may be postulated as the initial reaction:

$$Na_2S + NaOCl + H_2O = S + NaCl + 2NaOH$$

If the above reaction were the only reaction taking place, the ratio of equivalents of sodium hypochlorite to equivalents of sodium sulfide should be 1.
However, it was found that this ratio was not 1 but some value greater than 1 attaining 4 as a limit. It was further found that considerable sulfate is formed, and by analysis of the solutions (Tables 12 and 14), the increase in the ratio can be quantitatively shown to be entirely due to the formation of sulfate in any given solution.

As previously stated, regardless of the mechanism of the reaction, we may set down the following stoichiometric relations:

\[
\begin{align*}
\text{Na}_2\text{S} + \text{NaOCl} & \rightarrow \text{S} \quad \text{Ratio NaOCl/Na}_2\text{S} = 1 \\
\text{Na}_2\text{S} + 4\text{NaOCl} & \rightarrow \text{Na}_2\text{SO}_4 \quad \text{Ratio NaOCl/Na}_2\text{S} = 4
\end{align*}
\]

Obviously, if sulfate and sulfur are produced simultaneously (which fact has been established), the ratio will lie somewhere between 1 and 4, approaching these values as limits.

Since the primary reaction results only in the formation of sulfur, the formation of sulfate must depend upon some secondary reaction. The most logical explanation is the secondary reaction of the hypochlorite on the sulfur oxidizing it further to sulfate, but we are confronted with the fact that only part of the sulfur is oxidized, although there is at all times an excess of hypochlorite. It becomes necessary, therefore, to explain the oxidation of a portion of the sulfur to sulfate while a portion of it remains unoxidized.
In a study of the literature of sulfur reactions one finds quite frequent reference to the term "active" sulfur. This term, "active", sulfur, is usually applied to nascent sulfur, i.e. sulfur which has been set free by some chemical reaction presumably in the atomic state. A far greater reactivity is usually assigned to "active" sulfur than to ordinary sulfur. Referring again to Bullock and Forbes, we quote: "The reaction (sulfur and sodium hydroxide) takes place rather rapidly at elevated temperatures even with ordinary rhombic sulfur but at 25° the reaction is slow unless the sulfur is in an "active" state, set free by an oxidation of sulfide or in some similar way". "Active" sulfur is not a new concept but is found often in the older literature of sulfur reactions referred to as sulfur in status nascendi.

Here, it appears, is the explanation of the partial oxidation of the sulfur produced by the reaction:

\[ \text{Na}_2\text{S} + \text{NaOCl} + \text{H}_2\text{O} = \text{S} + \text{NaCl} + 2\text{NaOH} \]

The sulfur set free in the atomic state may react in two ways. It may combine with another atom of sulfur or it may be acted upon by a molecule of sodium hypochlorite. These two reactions may be written as follows:

(1) \[ \text{S} + \text{S} = \text{S}_2 \]

(2) \[ \text{S} + 2\text{NaOCl} + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{NaCl} \]

Reaction (1) is not, of course, limited to the formation of diatomic sulfur, but the diatomic molecule may react with another atom of sulfur, and so on forming colloidal sulfur.
Also reaction (2) is probably not kinetically correct since it is shown as a quinqueimolecular reaction. It can probably be represented more accurately by the following mechanism:

\[ S + \text{NaOCl} \rightarrow \text{SO} + \text{NaCl} \]
\[ \text{SO} + \text{NaOCl} \rightarrow \text{SO}_2 + \text{NaCl} \]
\[ \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \]
\[ \text{H}_2\text{SO}_3 + \text{NaOCl} \rightarrow \text{H}_2\text{SO}_4 + \text{NaCl} \]

Sulfur monoxide, SO, has recently been shown by Schenk (411) to be a primary oxidation product of sulfur.

To explain the experimental results, therefore, we may set down the following reactions as the determining factors from a kinetic standpoint:

\[ S + S = \text{S}_2 \]
\[ S + \text{NaOCl} \rightarrow \text{SO} + \text{NaCl} \]

If we are to explain the appearance of sulfate and sulfur as the reaction products from the above mechanism, we must assume that the two reactions have at least comparable rates of reaction; otherwise, one would take place to the exclusion of the other.

From the above equations it is evident that the speed of the first is proportional the square of the sulfur concentration and that of the second to the product of the concentration of the sulfur and the hypochlorite. It is further noted that the concentration of atomic sulfur at any time is a function of the initial sulfide concen-
tration. It would, therefore, be expected, qualitatively at least, that an increase of sulfide concentration would favor the formation of colloidal sulfur and on the other hand an increase in hypochlorite concentration should favor the formation of sulfate. This has been found to be experimentally true (Tables 15 and 19).

This mechanism also explains the apparent constancy of the ratio of hypochlorite to sulfide as long as the reactants are of practically the same concentration since, in this case, the square of the sulfur concentration is mathematically equivalent to the product of the concentration of the sulfur and hypochlorite and consequently the ratio of the velocity constants remains unchanged.

The mechanism appears to successfully explain variations due to changes in concentration but the effect of pH requires further study. It should be noted that the concentrations used in the above solutions will not give a wide divergence of pH and it so happened that the pH values of these solutions lay along the flat part of the pH curve. No very wide divergence of pH values is indicated by the apparent constancy of the ratio.

From the shape of the pH curve it would appear that there are two distinct forces at play reaching a minimum at a pH of about 10. We may consider this point as the ideal point where the above mechanism is a satisfactory explanation of the facts. However, to explain the increase
of sulfate formation both on the acid and basic side of pH of 10, it has been necessary to evolve two entirely different mechanisms which, however, will be seen to fit the experimental facts.

As previously shown sulfur and base react according to the equation:

$$6\text{NaOH} + 8\text{S} = 2\text{Na}_2\text{S}_3 + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$$

This equation represents a case of autoxidation and there is no net gain with respect to oxidation or reduction. The action of the base is to return the sulfur to solution in such a form that it is easily oxidized by the hypochlorite. It has been definitely shown (Table 20) that the action of hypochlorite on colloidal sulfur is too slow to have any effect on the final ratio as determined experimentally. Therefore, the increase in sulfate formation with increase in basicity of the solution can be explained by the following mechanism:

1. $$\text{S} + \text{S} = \text{S}_2$$
2. $$\text{S} + \text{NaOCl} = \text{SO} + \text{NaCl}, \text{etc. to sulfate}$$
3. $$8\text{S} + 6\text{NaOH} = 2\text{Na}_2\text{S}_3 + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$$
4. $$\text{Na}_2\text{S}_2\text{O}_3 + 4\text{NaOCl} + 2\text{NaOH} = 2\text{Na}_2\text{SO}_4 + 4\text{NaCl} + \text{H}_2\text{O}$$
5. $$\text{Na}_2\text{S}_2 + \text{NaOCl} + \text{H}_2\text{O} = 3\text{S} + \text{NaCl} + 2\text{NaOH}$$
6. $$\text{S} + \text{NaOH}, \text{etc.}$$

The first three reactions are the only ones necessary for a kinetic explanation of the course of the reaction. It is evident that as the basicity of the solution increases the rate of reaction (3) will increase while reactions (1)
and (2) will correspondingly diminish and it would appear that there would be a limiting basicity at which reaction (3) would take place to the exclusion of reactions (1) and (2). For the concentrations used in Table 33 it has been shown that this limiting value is 3 N with respect to base. It is also evident that, if reaction (3) takes place to the exclusion of (1) and (2), the final product will be sulfate. This has been found to be experimentally true. The agreement of experiment and postulate indicates that this mechanism satisfactorily explains the results.

In acid solution it is also found that there is an increase in the ratio indicating an increase in sulfate formation, but here it is necessary to evolve another mechanism for resolution of the sulfur since, there is insufficient hydroxyl ion concentration to employ the foregoing reactions.

As indicated in the review of the literature hypochlorous acid is a very weak acid. It is released from its salts by sodium bicarbonate which would suggest that free hypochlorous acid exists in solutions of comparatively high pH values, probably as high as 9 or 10. It has been shown that the minimum in the pH curve is at a pH value of around 10 which would indicate that at values below this we are dealing with free hypochlorous acid rather than sodium hypochlorite.

It is an established fact that hypochlorite has a greater oxidizing power in acid solution than it does in
basic solution. This greater oxidizing power is attributed to the presence of chlorine monoxide, Cl₂O. It has been proven that hypochlorous acid yields the following equilibria:

\[ \text{HOCI} \rightleftharpoons \text{OCl}^- + \text{H}^+ \quad K = 3.7 \times 10^{-8} \]
\[ 2\text{HOCI} \rightleftharpoons \text{Cl}_2\text{O} + \text{H}_2\text{O} \quad K = 9.6 \times 10^{-4} \]

and in the presence of HCl:

\[ \text{HOCI} + \text{HCl} \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O} \quad K = 2 \times 10^5 \]

If it is assumed that chlorine monoxide is the active agent in the resolution of sulfur it is not at once apparent from the above equilibria that an increase in hydrogen ion concentration would also increase the concentration of chlorine monoxide which would be required to satisfy the experimental results. Hypochlorous acid ionizes to such a small extent that addition of hydrogen ions to the solution would alter the concentration of hypochlorous acid to a negligible extent. It would appear that the addition of hydrogen ions in the presence of chloride ions (as is always the case in our solutions) would tend to decrease the concentration of hypochlorous acid by shifting the third equilibrium towards chlorine and water.

It is possible, therefore, that chlorine is the active agent in the resolution of sulfur by a mechanism similar to that given for basic solution since it has been shown that chlorine reacts slowly with sulfur at ordinary temperatures. However, this will not explain the fact that after colloidal sulfur has been formed in basic
solution, it will be rapidly redissolved upon acidification to a pH of two or less. It appears, therefore, that we must eliminate chlorine as playing any large part in the resolution of the sulfur.

Remington and Trimble (407) showed that the oxidation potentials of hypochlorite solutions were proportional to the hydrogen ion concentration of the solution, the greater the hydrogen ion concentration the greater the oxidation potential, and hence the greater the oxidizing power.

From our results we must postulate the existence of some oxidant which has a rapid action on colloidal sulfur. It has been shown that in the dry state chlorine monoxide reacts violently with sulfur with the formation of sulfur monochloride and sulfur dioxide. In aqueous solution both would probably be oxidized further to sulfuric acid.

The fact that an appreciable quantity of chlorine monoxide exists in very acid solutions can be shown by acidification of a solution of sodium hypochlorite with hydrochloric acid. Chlorine monoxide is quite easily distinguished by its odor which is similar to that of iodine. Considerable chlorine is also evolved but not in such large excess as to obscure the odor of chlorine monoxide.

There appears to be no logical way to explain the facts except to assume that the concentration of chlorine monoxide increases with increase of hydrogen ion concentra-
tration. This would explain the greater proportion of sulfate appearing as the pH decreases.

The following mechanism may, therefore, be proposed as that taking place in acid solution:

\[ \text{H}_2\text{S} + \text{HOC}_1 = \text{S} + \text{HCl} + \text{H}_2\text{O} \]
\[ \text{S} + \text{S} = \text{S}_2 \]
\[ 2\text{HOC}_1 = \text{H}_2\text{O} + \text{Cl}_2\text{O} \]
\[ \text{S} + \text{Cl}_2\text{O} = \text{SO} + \text{Cl}_2 \]
\[ \text{Cl}_2 + \text{H}_2\text{O} = \text{HOC}_1 + \text{HCl} \]
\[ \text{SO} + \text{HOC}_1 = \text{SO}_2 + \text{HCl} \]
\[ \text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3 \]
\[ \text{H}_2\text{SO}_3 + \text{HOC}_1 = \text{H}_2\text{SO}_4 + \text{HCl} \]

and in the limiting case where the second equation is negligible (pH of 2) the summation equation becomes:

\[ \text{H}_2\text{S} + 4\text{HOC}_1 = \text{H}_2\text{SO}_4 + 4\text{HCl} \]

It should be pointed out that the foregoing mechanisms both for acid and basic solution cannot be definitely set down as having been proved since there is no way of tracing the course of so rapid a series of reactions. From a kinetic point of view, however, the experimental results agree with these postulates.

Before concluding the discussion of the foregoing mechanisms it might be well to discuss the major reactions from the standpoint of free energy changes where the data is available. The free energy change of each of the reactions is calculated from data tabulated by Lewis and
Randall (410).

\[ S^\equiv + \text{OC1}^- + \text{H}_2\text{O} = S + \text{Cl}^- + 2\text{OH}^- \]

\[ \Delta F^\circ = -66,667 \text{ cal.}, \text{ if the free energy of the sulfur formed is considered to be zero} \]

\[ \Delta F^\circ = -36,427 \text{ cal.}, \text{ if the free energy of atomic sulfur is taken into consideration} \]

\[ \Delta F^\circ_{\text{atomic}} = 20,240 \text{ cal.} \]

\[ S + 2\text{OC1}^- + \text{H}_2\text{O} = \text{H}_2\text{SO}_3 + 2\text{Cl}^- \]

\[ \Delta F^\circ = -131,630 \text{ cal.}, \text{ if } \Delta F^\circ_{\text{S}} = 0 \]

\[ \Delta F^\circ = -162,920 \text{ cal.}, \text{ if } \Delta F^\circ_{\text{S}} = 30,240 \text{ cal.} \]

\[ S + S = \text{S}_2 \]

\[ \Delta F^\circ = -42,200 \text{ cal.} \]

\[ \text{H}_2\text{SO}_3 + \text{OC1}^- = \text{H}_2\text{SO}_4 + \text{Cl}^- \]

\[ \Delta F^\circ = -75,037 \text{ cal.} \]

\[ 4S + 6\text{OH}^- = 2\text{S}_2\text{O}_3^\equiv + 3\text{H}_2\text{O} \]

\[ \Delta F^\circ = -23,160 \text{ cal.}, \text{ if } \Delta F^\circ_{\text{S}} = 0 \]

\[ \Delta F^\circ = -144,120 \text{ cal.}, \text{ if } \Delta F^\circ_{\text{S}} = 30,240 \text{ cal.} \]

\[ \text{S}_2\text{O}_3^\equiv + 4\text{OC1}^- + 2\text{OH}^- = \text{SO}_4^{2-} + 4\text{Cl}^- + \text{H}_2\text{O} \]

\[ \Delta F^\circ = -332,380 \text{ cal.} \]

\[ \text{H}_2\text{S} + \text{HOC1} = \text{H}_2\text{O} + S + \text{HCl} \]

\[ \Delta F^\circ = -62,419 \text{ cal.}, \text{ if } \Delta F^\circ_{\text{S}} = 0 \]

\[ \Delta F^\circ = -32,179 \text{ cal.}, \text{ if } \Delta F^\circ_{\text{S}} = 30,240 \text{ cal.} \]
\[
S + 2\text{H}_2\text{OCl}^+ + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{Cl}^-
\]

\[
\Delta F^0 = -94,486 \text{ cal.}, \text{ if } \Delta F_B^0 = 0
\]

\[
\Delta F^0 = -124,708 \text{ cal.}, \text{ if } \Delta F_B^0 = 30,240 \text{ cal.}
\]

It is evident from the above that all of the equations present large negative values for the free energy change which indicates that the reactions take place spontaneously and that the equilibrium will be well in favor of the products. It should also be noted that in the reactions involving sulfur that there will be an increased free energy change if we consider the sulfur reacting as being in the "active" or atomic state.
CONCLUSIONS

It has been established that when excess hypochlorite reacts with sulfide, sulfur and sulfate are formed in amounts depending upon several variables, i.e. concentration of reactants, temperature, and pH of the reaction medium.

When the reactants are of approximately the same concentration, the relative amounts of sulfur and sulfate which are formed are approximately constant. If there is a wide divergence in the concentrations of the sulfide and hypochlorite, there is a corresponding difference in the ratio of sulfur to sulfate produced in the reaction. It has been found that high sulfide concentrations favor the formation of sulfur and high hypochlorite concentrations favor the formation of sulfate. The results have been shown to conform with the following mechanism; where the sulfur which enters into the secondary reaction is assumed to be "active" or nascent sulfur:

\[
\begin{align*}
\text{Na}_2\text{S} + \text{NaOCl} + \text{H}_2\text{O} & \rightarrow \text{S} + \text{NaCl} + 2\text{NaOH} \\
\text{S} + \text{S} & \rightarrow \text{S}_2 \text{, etc. to colloidal sulfur} \\
\text{S} + \text{NaOCl} & \rightarrow \text{SO} + \text{NaCl} \\
\text{SO} + \text{NaOCl} & \rightarrow \text{SO}_2 + \text{NaCl} \\
\text{SO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_3 \\
\text{H}_2\text{SO}_3 + \text{NaOCl} & \rightarrow \text{H}_2\text{SO}_4 + \text{NaCl}
\end{align*}
\]

The study of the effect of temperature on the reaction reveals the fact that high temperatures favor the formation of sulfate. At temperatures up to 50°, the plot of temperature against the ratio of equivalents of hypochlorite
reacting with a given number of equivalents of sulfide shows a straight line variation as would be expected, but at higher temperatures there is a rapid increase in the ratio showing increased production of sulfate. This may be explained by the rather rapid action of base on colloidal sulfur at high temperatures.

The ratio of equivalents of hypochlorite to equivalents of sodium sulfide plotted against the pH of the reaction medium reached a maximum of 4 (theoretical conversion to sulfate) at pH values of 2 or less and also in very basic solutions. There was a distinct minimum in the curve at a pH of about 10.

Increased production of sulfate on the basic side of the minimum is explained by the action of hydroxyl ion on "active" sulfur promoting autooxidation to sulfide and thiosulfate which are easily attacked by the hypochlorite. The mechanism in basic solution is represented as follows:

\[
\begin{align*}
Na_2S + NaOCl + H_2O & = S + NaCl + 2NaOH \\
S + S & = S_2, \text{ etc. to colloidal sulfur} \\
S + NaOCl & = SO + NaCl, \text{ etc. to sulfate} \\
3S + 6NaOH & = 2Na_2S_3 + Na_2S_2O_3 + 3H_2O \\
Na_2S_2O_3 + 4NaOCl + 2NaOH & = 2Na_2SO_4 + 4NaCl + H_2O \\
Na_2S_3 + NaOCl + H_2O & = 3S + NaCl + 2NaOH \\
S + NaOH, \text{ etc.}
\end{align*}
\]

In acid solution it was found necessary to propose a different mechanism to explain the increase in sulfate
production. This explanation involves the presence of chlorine monoxide. The mechanism in acid solution is represented as follows:

\[
\begin{align*}
H_2S + HOC1 &= S + HCl + H_2O \\
S + S &= S_2, \text{ etc. to colloidal sulfur} \\
2HOC1 &= H_2O + Cl_2O \\
S + Cl_2O &= SO + Cl_2 \\
Cl_2 + H_2O &= HOC1 + HCl \\
SO + HOC1 &= SO_2 + HCl \\
SO_2 + H_2O &= H_2SO_3 \\
H_2SO_3 + HOC1 &= H_2SO_4 + HCl
\end{align*}
\]

Below pH values of two, the second reaction is negligible and the summation of these reactions yields:

\[
H_2S + 4HOC1 = H_2SO_4 + 4HCl
\]

Where possible the reactions were studied from the standpoint of thermodynamics and it was shown by calculations of the free energy changes involved in the reactions, that they were all spontaneous.
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Lester Cole Faulkenberry was born March 27, 1911 at Columbia, South Carolina. He received his graded school education in the city schools of Columbia and graduated from Columbia High School in June, 1928. He entered the University of South Carolina in the Fall of 1928 and in June 1932 graduated with the degree of B.S. in Chemical engineering.

In the Fall of 1932 he came to Louisiana State University as a Graduate Fellow in Chemistry and in June, 1934 received the degree of Master of Science. He continued his graduate study as Graduate Assistant during the session 1934-35 and in the Fall of 1935 was appointed Research Fellow for the Freeport Sulphur Company. He is now a candidate for the Degree of Doctor of Philosophy.
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