352. *The Oxidation of Sulphurous Acid.*

By Henry Bassett and William G. Parker.

The oxidation of sulphurous acid by oxides of manganese, by ferric and cupric salts, and by molecular oxygen in presence of various dissolved salts has been studied with special reference to the proportions of sulphate and dithionate which are formed.

Oxidation by the solid oxides occurs on the surface and, while the proportion of dithionate formed is specific for each polymorph, it is independent of practically all other factors. Dithionate can only be formed when an oxide is reduced in one-electron steps. It can be formed with the oxides of manganese owing to the well-defined ter- and quadri-valent stages of the metal. It depends on surface adsorption of SO_3'' ions : either they are discharged successively in two single-electron steps to form sulphate or, alternatively, two of them after partial discharge unite to form S_2O_6''. The lattice structure of the individual oxide determines the extent to which these two modes of oxidation of the adsorbed SO_3'' will occur.

Ferric hydroxide dissolves before it is reduced by sulphurous acid, so that the mechanism is somewhat different in this case and involves a complex ferrisulphite anion. Oxidation of the sulphite to dithionate is almost quantitative, and the same applies to oxidation by ferric sulphate and ferric nitrate. Ferric chloride gives a much smaller proportion of dithionate, and very little in presence of hydrochloric acid, which is connected with the high stability of ferrichloride anions.

It seems clear that the oxidation of sulphurous acid by molecular oxygen follows a chain mechanism, but that which is usually accepted (due to Franck and Haber, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1931, 250) is inadequate to explain the variety of effects observed when this oxidation occurs in presence of salts. The Franck–Haber chain mechanism for the uncatalysed oxidation can be improved by assuming that the oxygen reacts in the form of ionic complexes such as $[O_2 \rightarrow SO_3]''$ and $[O_2 \rightarrow S_2O_5]''$.

The enormously accelerated oxidation caused by manganese ions is attributed to the formation of complex sulphite ions carrying co-ordinated oxygen molecules such as $[O_2 \rightarrow Mn(SO_3)_2]''$ which rapidly undergo self-oxidation and -reduction. Cobalt, nickel, and ferrous iron can give rise to similar but less active complexes.

Assumption of these two types of oxygen addition complexes enables satisfactory explanations to be given of all the peculiar results obtained when sulphurous acid is oxidised by molecular oxygen in presence of salts.

Concentrated sulphurous acid solution was oxidised in three different ways, and the work is presented accordingly in three parts as follows :

1. Oxidation by oxides of manganese.
2. Oxidation by ferric and cupric salts.
3. Oxidation by free oxygen in the presence of dissolved salts.

Dithionic acid as well as sulphuric acid may be formed in the oxidation of sulphurous acid by air and other oxidising agents. Dithionic acid, which is very stable towards oxidation, is an individual product and not an intermediate stage in the formation of sulphuric acid. It follows therefore that these two acids are derived from sulphurous acid by independent reactions, and the principal object of this work was to examine the change in the relative quantities of sulphate and dithionate formed by each oxidation in an attempt to determine the mechanisms of these reactions. The work is a continuation of that by Bassett and Henry (*J.*, 1935, 914).

Concentrated sulphurous acid solutions were used throughout, partly because they were relatively reproducible and easily prepared by saturating the aqueous solutions with sulphur dioxide at the temperature of the experiment, and partly because such solutions were needed to reduce some of the natural oxides sufficiently rapidly (Part 1) and to obtain a reasonable proportion of dithionate in the uncatalysed oxidation by molecular oxygen (Part 3).

1. OXIDATION BY THE OXIDES OF MANGANESE.

Review of the Literature.—Dithionic acid was first prepared by Gay-Lussac and Welter (*Ann. Chim. Phys.*, 1819, **10**, 312) who passed sulphur dioxide through water containing manganese dioxide in suspension. Heeren (*Pogg. Annalen*, 1826, **7**, 55), by the same method and using finely ground "grau Braunstein" (*i.e.*, pyrolusite, MnO_2), found that some sulphate was always formed, in amount varying from 0·370 to 0·135 part of H_2SO_4 to 1 part of $H_2S_2O_6$. Berzelius ("Lehrbuch," Dresden, 1825, Vol. II, p. 467), without giving experimental evidence, attributed the sulphate formation to "oxyd-hydrat" (*i.e.*, Mn_2O_3,H_2O) which he considered was always present as impurity in the pyrolusite. He thought that pure manganese dioxide gave only dithionate. Heeren tested this point by determining the weight of oxide dissolved, as well as the amounts of sulphate and dithionate formed. The weight of oxide dissolved was always considerably less than that required by Berzelius's theory, so Heeren concluded that some of the sulphate must have been formed by oxidation by MnO_2, the equivalent weight of which is much less than that of the requisite amount of Mn_2O_3,H_2O.

Heeren also examined the action of sulphurous acid on finely ground "glanz-Braunstein" (*i.e.*, manganite, natural Mn_2O_3,H_2O) and on a freshly precipitated "oxyd-hydrat" purified by means of very dilute nitric acid. The action on the mineral was very slow but in the case of the precipitated oxide some dithionate was formed. He attributed the varying proportions of dithionate to sulphate obtained in his experiments to three factors: (1) temperature—high temperatures caused high yields of sulphate by decomposition of dithionate; (2) presence in the dioxide of Mn_2O_3,H_2O which gave more sulphate than dithionate; and (3) state of division of the oxide—the finer the oxide the greater the yield of dithionate. Spring and Bourgeois (*Bull. Soc. chim.*, 1886, **46**, 151; Spring, "Collected Researches," p. 1123), from experiments with powdered pyrolusite and with freshly precipitated oxides, came to exactly the opposite conclusion as to the influence of the state of division.

All this earlier work suffers from two defects: (*a*) no analyses, and in particular no determinations of the available oxygen, appear to have been made of either the natural or the artificially prepared oxides which were used in the experiments; and (*b*) the marked effect of manganese salts in catalysing oxidation of sulphurous acid by molecular oxygen was probably not known or appreciated and was neither guarded against nor allowed for.

The formation of a red solution when sulphur dioxide is passed into a suspension of ferric hydroxide was first noticed by Berthier (*Ann. Chim. Phys.*, 1843, **7**, 78) and the presence of ferric sulphite in this solution was confirmed by Seubert and Elten (*Z. anorg. Chem.*, 1893, **4**, 86). The red solution becomes pale green when kept, and ferrous sulphite and dithionate are formed (Gélis, *Bull. Soc. chim.*, 1863, **5**, 333; *Ann. Chim. Phys*, 1862, **65**, 222). J. Meyer (*Ber.*, 1901, **34**, 3606) assumed that the course of the reaction with manganese dioxide was similar, *viz.*: $2MnO_2 + 3H_2SO_3 = Mn_2(SO_3)_3 + 3H_2O + O$; $Mn_2(SO_3)_3 = MnSO_3 + MnS_2O_6$; $MnSO_3 + O = MnSO_4$. Carpenter (*J.*, 1902, **81**, 1) endeavoured to trace a connection between the yields of dithionate obtained from hydroxides of the iron group and their heats of reduction.

Several early workers observed that no dithionate was formed when the peroxide of lead, barium, magnesium, or sodium reacted with sulphurous acid. Luigi Marino (*Z. anorg. Chem.*, 1907, **56**, 233) confirmed this for the peroxides of lead and barium whereas with pure MnO_2 he obtained dithionate plus a little sulphate which he supposed was formed by an "induced" reaction: $MnO_2 + 2SO_2 = MnS_2O_6$ (main reaction); $MnS_2O_6 + MnO_2 = 2MnSO_4$ ("induced" reaction). The differing behaviour of the peroxides was ascribed to differences in their constitution.

After this date little work has been recorded on the reaction of oxides of manganese with sulphurous acid but some important work has been done on their constitution.

It is necessary to consider what is known about the structures of the oxides of ter- and quadri-valent manganese before the oxidation of sulphurous acid by these compounds can be profitably discussed.

The Natural Oxides.—A study, with *X*-ray examination, of manganese oxide minerals has been published by Fleischer and Richmond (*Econ. Geology*, 1943, **38**, 269).

Pyrolusite, MnO_2, crystallises in the tetragonal system with the rutile type of structure (Ferrari, *Atti R. Accad. Lincei*, 1926, **3**, 224). There is always a slight deficiency of oxygen. The manganese is quadrivalent.

Ramsdellite is an orthorhombic form of MnO_2, first described by Ramsdell (*Amer. Min.*, 1932, **17**, 143; see also Fleischer and Richmond, *loc. cit.*).

Manganite, Mn_2O_3,H_2O, is monoclinic and belongs to the boehmite–lepidocrocite group. The arrangement of the manganese atoms in the crystal suggests equal valencies of three. More value must be attached to this result than to the suggestion of a mixed two and four valency given by the behaviour of the compound with acids, though this view of its structure is supported by Krishnan and Banerjee (*Trans. Faraday Soc.*, 1939, **35**, 385).

Hausmannite is tetragonal and a pseudo-spinel. Chemical and electrochemical behaviour support the view that the manganese is bi- and ter-valent (MnO,Mn_2O_3) rather than bi- and quadri-valent.

Braunite occurs massive and also as dark brownish-black or steel-grey crystals. Combined silica is probably always present and on account of this the accepted formula for the mineral is $3Mn_2O_3,MnSiO_3$.

Oxides of Manganese prepared artificially.—Great care must be taken in drawing conclusions as to the structures of the oxides of manganese either from oxygen-pressure curves or from *X*-ray diagrams. Drucker and Huttner (*Z. physikal. Chem.*, 1928, **131**, *A*, 237) showed that the oxygen-pressure curves varied within certain limits with the physical condition of the oxide. Oxides prepared in a dry way are usually well crystallised, while those obtained by a wet method are amorphous or poorly crystalline. Le Blanc and Wehner (*Z. physikal. Chem.*, 1934, **168**, *A*, 67) found that the MnO structure persisted up to $MnO_{1\cdot13}$, that of Mn_3O_4 up to $MnO_{1\cdot42}$, and that of Mn_2O_3 up to $MnO_{1\cdot58}$, and this complicates the interpretation of powder diagrams. MnO_2, however, though normally slightly deficient in oxygen, cannot lose more without the appearance of the Mn_2O_3 lattice. Dubois (*Compt. rend.*, 1934, **199**, 1416; 1935, **200**, 1107) established the existence of at least two polymorphs of MnO_2 and of Mn_2O_3. The oxide obtained by heating manganese nitrate gave an *X*-ray diagram identical with that of pyrolusite, and this oxide he called β-MnO_2. The oxides formed by spontaneous decomposition of $HMnO_4$ and by reduction of permanganate solution with manganese sulphate gave, after repeated washing with hot nitric acid, $MnO_2,0\cdot88H_2O$ and $MnO_2,1\cdot66H_2O$ respectively. They had identical *X*-ray diagrams, quite different from that of pyrolusite. Dubois called this α-MnO_2. Evidence for a third polymorph was also given but was not conclusive. Glemser (*Ber.*, 1939, **72**, 1879) obtained $MnO_{1\cdot97}$ by wet methods very similar to those used by Dubois (*loc. cit.*), which may be correlated with Dubois's α-MnO_2 although Glemser called it γ-MnO_2 and said that its *X*-ray diagram was not identical with that given by Dubois for his α-MnO_2.

α-MnO_2 is reduced by hydrogen to Mn_2O_3 at 170°, and the β-MnO_2 at 220°. The Mn_2O_3 is further reduced at 260° (Dunoyer, *Compt. rend.*, 1939, **208**, 1018). Both α- and β-MnO_2 above 600° in oxygen or nitrogen yield β-Mn_2O_3 (see below). Dehydration in air of the dimanganese trioxide prepared by oxidation of manganese sulphate with hydrogen peroxide in alkaline solution (Carnot, *Compt. rend.*, 1888, **107**, 999, 1150) is accompanied by some oxidation. Above 600° a form of Mn_2O_3 is obtained, giving very clear *X*-ray pictures, which Dubois (*loc. cit.*) called β-Mn_2O_3.

The initial precipitate obtained by the hydrogen peroxide method looks amorphous but gives a good *X*-ray diagram identical with that of manganite. On exposure to air at room temperature the precipitate loses water slowly and approaches the composition required by Mn_2O_3,H_2O. When this material is heated to 100° *in vacuo*, this composition is passed through as a definite stage, but more water is easily lost below 250°, or even a little above 100°, to give Mn_2O_3 without any dioxide. Dubois called this variety of the oxide α-Mn_2O_3 as it is quite different from the β-Mn_2O_3 obtained at 600° and into which it passes on heating to this temperature.

Mn_3O_4 has not been prepared in a pure state by a wet method. Thermal decomposition of the higher oxide, nitrate, carbonate, or oxalate at appropriate temperatures yields crystalline products having the same composition and *X*-ray structure as hausmannite.

Dubois's β-Mn_2O_3 and bixbyite, $(Mn,Fe)_2O_3$, are isometric and have the *C*-structure typical of certain sesquioxides (Zachariasen, *Norsk Geol. Tidskr.*, 1927, **9**, 310). All the manganese in bixbyite, and therefore in β-Mn_2O_3, is six-co-ordinated and tervalent.

Braunite is tetragonal, although Le Blanc and Wehner (*loc. cit.*) stated that bixbyite from Dugdale Range, Utah, and braunite from Oehrenstock near Ilmenau gave identical *X*-ray diagrams.

Verwey and De Boer (*Rec. Trav. chim.*, 1936, **58**, 531) have shown that Dubois's α-Mn_2O_3 has the hausmannite structure with vacant lattice positions. It is related to hausmannite as γ-Fe_2O_3 is to Fe_3O_4 and would be expected therefore to contain only tervalent manganese. In spite of this Verwey and De Boer suggest that hausmannite is $Mn^{II}{}_2Mn^{IV}O_4$ because of its electrical conductivity rather than $Mn^{II}Mn^{III}{}_2O_4$.

There seems to be little doubt from the *X*-ray work carried out on the compounds that braunite is structurally much more closely related to bixbyite and β-Mn_2O_3 than to hausmannite and α-Mn_2O_3. The part played by the silica in braunite is still obscure. It would be possible, if conditions were otherwise suitable, for a Mn^{III} atom in a compound ($Mn^{III}{}_2O_3$) to be replaced by a silicon atom if at the same time another Mn^{III} atom were replaced by Mn^{II}. Now, in the *C*-type oxide structure to which bixbyite and β-Mn_2O_3 belong, all the metal ions are six-co-ordinated. In silicon–oxygen structures the silicon is normally in four co-ordination, but it can enter into six co-ordination as in the fluorosilicates. It seems possible that braunite may be derived in this manner from β-Mn_2O_3, but that some distortion of the lattice is caused and a limit set to the extent of the replacement of manganese by silicon (*a*) by the unusual co-ordination of the silicon and (*b*) by the fact that the ionic character of the silicon–oxygen links is rather low for a structure which is essentially ionic. It is not easy to say whether the accepted formula for braunite, $3Mn_2O_3,MnSiO_3$, is exact or only approximate.

The number of polymorphs of MnO_2 and Mn_2O_3 which exist still appears to be somewhat uncertain while views still differ as to their structures (Fleischer and Richmond, *loc. cit.*; Imperial Institute Ann. Report, 1946, p. 31; Fyfe, *Nature*, 1949, **164**, 790; see also *Ann. Reports*, 1949, **46**, 73).

An unfortunate complication has been introduced into the nomenclature of the polymorphs. It has arisen from the recognition that Dubois's low-temperature or α-form of Mn_2O_3 is related to the pseudo-spinel hausmannite, Mn_3O_4, in the same way that γ-Fe_2O_3 is related to the spinel Fe_3O_4. Its structure does appear to be fundamentally similar to that of γ-Fe_2O_3 and γ-Al_2O_3 although probably tetragonal rather than cubic (Le Blanc and Wehner, *loc. cit.*). Dubois's α-Mn_2O_3 is now sometimes called γ-Mn_2O_3 for this reason and this has led to his β-Mn_2O_3 being called α-Mn_2O_3 which is unsatisfactory since it is body-centred cubic and does not correspond to α-Fe_2O_3 or α-Al_2O_3 which are hexagonal. It would appear better, on the whole, to retain Dubois's original nomenclature for the forms of Mn_2O_3 and this has been done in the present paper. The case illustrates the great difficulty in finding a satisfactory nomenclature for polymorphs.

EXPERIMENTAL.

Oxides of Manganese used in the Present Investigation. See Table II.—*Manganese dioxide.* (1) Pyrolusite, purchased, source unknown.

(2) Pyrolusite, purchased as manganite from Nova Scotia but found to be pyrolusite of high purity.

(3) Pyrolusite of good commercial grade, supplied as small pellets.

(4) (*a*) Manganese nitrate was heated to about 200°. The oxide produced was treated with concentrated nitric acid, washed, and dried for 3 hours at 100°. (*b*) Manganese nitrate (AnalaR standard) was heated to 154° under reduced pressure (20 mm. of Hg.) The oxide was washed free from nitrate and dried for 3 hours at 100°. This method (Krull, *Chemie der Erde*, 1932, **7**, 473) gives a minutely crystalline form of manganese dioxide.

(5) (*a*) and (*b*). Two preparations by the same method. Powdered potassium permanganate was slowly added to well stirred concentrated nitric acid at 0°. Stirring was discontinued after 3 hours but the mixture was kept for 2 days before collection of the oxide on a sintered glass funnel. This was a black, finely divided, product which filtered easily. It was used in the wet state and also after being dried at 96° for 3 hours.

(6) Manganese chloride solution was added to an excess of sodium carbonate solution, and chlorine bubbled through the mixture. The manganese dioxide formed was filtered off, washed, treated with dilute nitric acid, and again washed. It was used in the wet state and also after being dried at 96° for 3 hours.

(7) A 0·5M-solution of manganous sulphate, about 0·1N. with sulphuric acid, was electrolysed at 70°, at platinum electrodes (van Arsdale and Maier, *Trans. Amer. Electrochem. Soc.*, 1918, **33**, 109). The anode was a fine gauze, 4 sq. in. in area; a current of 0·4 amp. at 4 volts was used. After 10 hours a good yield of oxide had formed on the anode as a dense lustrous black film.

(8) Purchased precipitated MnO_2 of " AnalaR " quality.

Dimanganese trioxide. (9)(*a*) Manganite from Ihlefeld, Harz Mountains, one of the type localities for this mineral. This was a glistening black crystalline mineral, which on being ground gave a chocolate-brown powder. (*b*) Some of the same manganite was heated in air for an hour at 600°.

(10) Braunite from Ilmenau, Thuringia. This was a steel-grey crystalline mass containing patches of quartz. The combined silica content (9·5%) agreed very closely with that required for $3Mn_2O_3,MnSiO_3$ and so did the available oxygen.

(11) Manganese dioxide prepared as in 4(*b*) was heated at 550° in a slow current of oxygen for 4 hours. There was no change in the appearance of the oxide.

(12) Preparation (8) was heated at 900° in an air current for 3 hours. The oxide lost 12·6% in weight but there was no change in colour.

(13) 50 C.c. of 0·2N-ammonia were added in the cold with stirring to a mixture of $MnSO_4,4H_2O$ (2 g.) in water (350 c.c.) and 2N-hydrogen peroxide (100 c.c.). The mixture was heated rapidly to the b. p. and kept there for 4 minutes. The oxide filtered satisfactorily and was washed and then dried *in vacuo* at 100°.

Trimanganase tetroxide. (14) Hausmannite from Bigrigg, Cumberland. The steel-grey crystals gave a reddish-brown powder on being ground.

(15) Ground pyrolusite [sample (2)] was heated to 950—1000° for 3 hours in a slow air current. There was no change in appearance.

(16) Manganese dioxide, prepared as in 4(*b*), was heated to 950—1000° for 2 hours in a slow current of air. The oxide lost 14·9% in weight and became reddish-brown.

(17) Manganese dioxide, prepared as in (6), was heated to 200° in a slow current of hydrogen. The oxide was rapidly reduced to a greenish product.

Analysis of Oxides of Manganese.—The manganese content was determined by the phosphate method. The available oxygen was determined in two ways : (*a*) by Bunsen's method in an all-glass apparatus through which a stream of carbon dioxide carried the chlorine evolved into cold acidified potassium iodide solution; and (*b*) dissolving the oxide in excess of standardised sodium oxalate solution acidified with sulphuric acid, and back-titration with standard permanganate (Lunge, " Sulphuric Acid and Alkali," 2nd edn., 1896, Vol. III, p. 274). Bunsen's method generally gave somewhat lower values for the available oxygen than did Lunge's method and this was traced to oxidation of oxalate by atmospheric oxygen catalysed by the manganese salt. The following results illustrate this effect.

Experimental conditions.	Titre (c.c.) with 0·1N-$KMnO_4$.
Acidified sodium oxalate (25 c.c.) was heated to 60° and titrated immediately.........	28·6
The oxalate solution, plus manganese sulphate (0·3 g.), was heated to 95° and titrated immediately	28·6
As in the preceding case but kept at 80—90° for 2 hours and then titrated..............	27·5
As in the preceding case but in an atmosphere of CO_2..	28·6
Two estimations of some pyrolusite made by dissolving the mineral as rapidly as possible in sodium oxalate solution at 60° gave 0·99 and 0·98 atom-equiv. of available oxygen respectively.	
Two estimations of the same pyrolusite by sodium oxalate in an atmosphere of CO_2 gave 0·97 atom-equiv of available oxygen in both cases.	
Analysis of the same pyrolusite by the Bunsen method gave 0·94 atom-equiv. of available oxygen.	

Hot acidified sodium oxalate alone is not oxidised by air, even on fairly long exposure, but the presence of manganese sulphate catalyses the oxidation. The precipitated dioxides which dissolved readily, and in most cases in the cold, and the pyrolusite which was estimated in an atmosphere of carbon dioxide, gave values which were consistently 3% higher than the corersponding values obtained by the Bunsen method. Under the conditions of the analyses it was estimated that dissolved oxygen could lead to an error of 2·7% and this appears to provide a reasonable explanation of the discrepancy between the two methods.

Clearly, estimation by the sodium oxalate method of the available oxygen in manganese oxides is valueless unless it is made in an oxygen-free atmosphere and with sodium oxalate solution prepared with well-boiled water. Only results obtained by Bunsen's method are given in Table II.

Bhatnagar and his co-workers (*J.*, 1939, **1441**) obtained good agreement between the two methods but no details of the procedures or of any precautions were stated. Schroder (*Z. off. Chem.*, 1910, **16**, 270) studied Lunge's method for the estimation of available oxygen in pyrolusite. His results were high and he showed that even the titration of oxalic acid with potassium permanganate suffered a small error owing to induced atmospheric oxidation when the titration was slow (5—10 minutes), and the error was greatly increased by the presence of manganese salts, even in strongly acid solution titrated rapidly.

Before examining the oxidation of sulphurous acid by the various oxides of manganese it was necessary to determine the constancy of the results for any one oxide.

Effect of concentration. The effect of variation in concentration of the sulphurous acid, on the proportion of dithionate to sulphate in the oxidation products, was found to be negligible over a wide range for concentrated solutions but in dilute solutions the proportion of dithionate formed appears to be lower (Table I*a*).

Effect of temperature. The solubility of sulphur dioxide in water was found by Freese (*Chem. Ztg.*, 1920, **44**, 294) to be 228·3 g./l. at 0°, 94·1 at 25°, and 54·1 at 40°. The concentration of the saturated solutions does not fall below 1·7N. even at 40°, and such a change would not influence the products of oxidation. Furthermore Spring and Bourgeois (*loc. cit.*) showed that dithionic acid is not rapidly decomposed below 75°. It could reasonably be assumed that, unless the mechanism of the oxidation was affected by temperature, close temperature control of the solutions was unnecessary. This was borne out by experiment (Table 1*b*).

Particle size was also found to be without influence on the yield of dithionate (Table 1*c*).

TABLE I.

(*a*) *Effect of concentration of* H_2SO_3 *solution at* 25°.

Prep. no. (see Table II).	Normality of H_2SO_3 solution.	Yield of dithionate, %.	Prep. no. (see Table II).	Normality of H_2SO_3 solution.	Yield of dithionate, %.
1 (Pyrolusite) ...	3	96	8 (Precipitated MnO_2)	3	77
,, ...	2	95	,,	0·01	64
,,	1	96			

(*b*) *Effect of temperature.*

Prep. no. (see Table II).	Temp. of saturated H_2SO_3 solution.	Yield of dithionate, %.
5(*b*) (Precipitated oxide in wet state) ...	0°	38
,, ,, ,, ,, ...	25	36
,, ,, ,, ,, ...	40	36

(*c*) *Effect of mechanical grinding on the behaviour of an oxide.*

Treatment of pyrolusite No. 3 (see p. 1543).	Time to dissolve similar quantities in saturated H_2SO_3 solution.	Yield of dithionate, %.
(1) Pellets rough ground in a porcelain mortar	60 hr. (approx.)	96
(2) Ground oxide from (1) was ground wet for an hour in an agate mortar	24 ,,	96
(3) Pellets ground in a ball mill (work kindly arranged by Dr. Taylor of I.C.I., Ltd., Billingham). This material was at least twice as fine as the agate-ground material ...	6 ,,	96

The results of these preliminary experiments show that the behaviour of an oxide is not determined by the changes in the conditions described. Anomalies recorded by earlier workers were most probably caused by the method used. No mention is made of the use of an inert atmosphere and it may be assumed that the solutions were in contact with air for widely varying times—evidently the strongly catalytic effect of manganous salts on the oxidation of H_2SO_3 by air was not considered. The magnitude of this effect in the production of sulphate, and sulphate only, is shown in Part 3 of this work and again in Table II of the present Part, where the amount of air-oxidation is calculated for each of the oxide reactions. These reactions did not take place in contact with air, although all trace of air was not rigidly excluded. Moreover, the speed of the catalysed reaction increases with rise of temperature. If allowance is made for this additional reaction, the results of Heeren and others may be explained. For example, Heeren obtained less sulphate when the oxide was more finely divided because it reacted in a shorter time and was accompanied by less air-oxidation. Again, the sulphate yield at higher temperatures was always higher because the rate of the subsidiary reaction had greatly increased. Spring and Bourgeois recorded two experiments with sulphurous acid solution at 21—22°, in which finely ground pyrolusite produced more sulphate than coarse lumps of the same mineral. This result can only be explained if it is assumed that in the experiment with the fine material the solution was in contact with the air for a longer period than in the other case.

The following procedure was adopted for all the oxides investigated by us. 80 C.c. of distilled water were saturated with sulphur dioxide at room temperature in a 160-c.c. Dreschel bottle and 0·2—0·4 g. of the oxide was added. The bottle was closed and shaken at intervals until the oxide had dissolved. The bottle was cooled in water in those cases where dissolution of the oxide occurred rapidly, to prevent any large rise of temperature. Sufficient hydrochloric acid was then added to decompose any manganese sulphite and a current of carbon dioxide was passed through the solution until no trace of sulphur dioxide remained, a final test being made with iodine and starch paste. After dilution to 200 c.c., manganese, sulphate, and dithionate were determined in separate portions, the dithionate after removal of the sulphate, and manganese with barium hydroxide. Details are given in Part 3.

To calculate the proportion of sulphur dioxide oxidised to dithionate by the oxide, the amount of dithionate formed and the manganese content of the solution alone were used. The results of the catalysed reactions described in Part 3 indicate clearly that oxidation of sulphurous acid solution by free oxygen in the presence of manganese salts gives sulphate only and that the quantity of dithionate formed is negligible. The dithionate found in the analysis must therefore arise entirely by oxidation by the manganese oxide, and the amount of oxygen required could be calculated and deducted from the amount of oxygen known to be available from the manganese content of the solution and the analysis of the oxide already made. The sulphate formed was calculated from the remainder of the available oxygen. In this way the sulphate arising from oxidation by dissolved air and any air contained in the space above the solution was not included.

It is now possible to consider the oxidation of sulphurous acid by various oxides of manganese. Analysis of these oxides, whether natural or artificially prepared, showed that none of them corresponded exactly to the nominal compounds MnO_2, Mn_2O_3, or Mn_3O_4. The discrepancy was particularly marked with manganese dioxides. The best pyrolusite sample was $MnO_{1\cdot94}$, and an oxide formed by thermal decomposition of manganese nitrate had a similar proportion of available oxygen. Precipitated oxides, with the exception of an electrolytic preparation, gave lower values for the oxygen content. Treatment of an oxide with hot nitric acid increased the proportion of oxygen in the compound, and according to the literature many repetitions of this treatment will give ultimately $MnO_{2\cdot0}$.

TABLE II.

Oxidation of sulphurous acid by the oxides of manganese. Proportion of dithionate formed.

No. of prep. (p. 1543).	MnO_x: value of *x*, Bunsen method.	Probable nature of oxide.	Mn content of the solution as NH_4MnPO_4,H_2O, g.	$BaSO_4$ (g.) from			SO_2 (%) oxidised to S_2O_6'' by oxide.
				S_2O_6''.	SO_4''.		
				Oxidation by the oxide.		air-oxidation.	
A. Manganese dioxides.							
1	1·92	MnO_2	0·1227	0·2731	0·0065	0·0096	97·7
2	1·94	MnO_2	0·1068	0·1204	0·0056	0·0069	95·6
4(*a*)	1·93	MnO_2	0·2544	0·5506	0·0217	0·0308	92·2
4(*b*)	1·84	MnO_2	0·0793	0·1519	0·0078	0·0080	95·1
5(*a*) (1) Wet	1·87	Amorphous	0·895	0·303	0·813	0·077	27·2
5(*a*) (2) Dried	,,	MnO_2	1·331	1·826	0·520	0·125	77·8
5(*b*) (1) Wet	1·85	Amorphous	0·1950	0·0898	0·1626	0·0313	35·6
5(*b*) (2) Dried	,,	MnO_2	0·0838	0·1041	0·0372	0·0504	73·7
6(1) Dried	1·76	Mixture of MnO_2 and amorphous	0·1280	0·1083	0·0621	0·0242	63·6
6(2) Dried	1·76	MnO_2	0·2104	0·2399	0·0808	0·0650	74·8
7	1·95	MnO_2	0·2446	0·3834	0·1000	0·0142	79·3
8	1·91	MnO_2	0·3482	0·4947	0·1505	0·0415	76·7
B. Dimanganese trioxides							
9(*a*)	1·53	Manganite	0·1901	0·1189	0·0666	0·0074	64·1
9(*b*)	1·51	β-Mn_2O_3	0·1242	0·1382	0·0103	0·0501	93·1
10	1·42	Braunite	0·3243	0·2858	0·0282	0·1155	91·0
11	1·51	β-Mn_2O_3	0·2034	0·2340	0·0137	0·0108	94·5
12	1·42	Mixture of β-Mn_2O_3 and Mn_3O_4	0·2468	0·1894	0·0398	0·0040	82·6
13(1) Before drying	1·41	Manganite structure	0·3693	0·1670	0·1085	0·0235	60·6
13(2) After drying	1·41	α-Mn_2O_3	0·2511	0·1832	0·0390	0·0111	82·5
C. Trimanganese tetroxides.							
14	1·32	Hausmannite structure	0·3224	0·1674	0·0467	0·0420	78·2
15	1·36	,,	0·2319	0·1523	0·0363	0·1050	80·7
16	1·34	,,	0·2463	0·1218	0·0441	0·0159	73·4
17	1·18	,,	0·2638	0·0620	0·0183	0·0043	77·2

Discussion.—While the results (Table II) show that all the oxides do not produce the same proportion of dithionate in this reaction, it is possible to group the oxides according to their dithionate yields.

The manganese dioxides form three groups according to the dithionate yield, *viz.* : (1) 95—97% : pyrolusites and oxide produced by thermal decomposition of manganese nitrate; these belong to Dubois's β-MnO_2 group. (2) 74—79% : oxides prepared by a wet method and dried at a moderate temperature (96°), together with an oxide prepared electrolytically : this is probably α-MnO_2, as are the other members of this set. (3) Low and variable percentages : oxides freshly precipitated and used immediately in the wet state. These oxides are probably amorphous or only partly crystalline at this stage, and the amount of dithionate varies according to the extent to which crystal formation has occurred. Dissolution of these oxides was extremely rapid and may have taken place before reduction, so that the reaction was perhaps not entirely a surface reaction.

The dimanganese trioxides also form three groups, *viz.* : (1) 91—95% : braunite and oxides formed from the dioxide or manganite at approx. 600°. (2) 60—64% : manganite and one precipitated oxide [No. 13 (1) in Table II]. (3) 82—83% : two oxides, one formed by precipitation and the other by heating a dioxide in air at 900° [No. 13 (2) and No. 12 respectively in Table II]. No. 13 (2) had lost nearly all its water and should therefore have been mainly α-Mn_2O_3. No. 12 was probably a mixture of β-Mn_2O_3 and Mn_3O_4, since α-Mn_2O_3 is not stable at 900°

The trimanganese tetroxides form a single group, and this is in agreement with theory since only one form of the oxide is known. The yield of dithionate from this oxide, approximately 80%, is close to the yield from α-Mn_2O_3.

All these groups appear to be well defined, having regard to the limits of accuracy of the dithionate determination and the nature of the oxides. Any explanation of the mechanism of the oxidation must be compatible with them.

Sulphurous acid solution may be assumed to contain SO_2, SO_3'', S_2O_5'', H_2SO_3, $H_2S_2O_5$, HS_2O_5', and HSO_3' in amounts depending on the acidity and the total SO_2 concentration. Of these, SO_2, HSO_3' and SO_3'' have been identified by spectroscopy (Albu and Goldfinger, *Z. physikal. Chem.*, 1932, **16**, *B*, 338). In the oxidation of the solution by manganese dioxide, if the reduction $Mn^{4+} \longrightarrow Mn^{2+}$ occurred in a single step through the discharge of the doubly charged anions SO_3'' and S_2O_5'', the resulting neutral molecules would immediately react with water to form H_2SO_4 and $H_2S_2O_6$ respectively. The quantity of dithionate produced in this way is probably negligible since the concentration of S_2O_5'' ions is relatively small, and in the analogous reaction with PbO_2, which must occur in a single stage involving two electrons, very little dithionate is formed. It was suggested therefore by Bassett and Henry (*J.*, 1935, 914) that the large yield of dithionate in the oxidation by MnO_2 might be caused by reduction occurring in two steps through the well-defined tervalent state of manganese. Thus, in either the first step $Mn^{4+} \longrightarrow Mn^{3+}$ or the second step $Mn^{3+} \longrightarrow Mn^{2+}$, a single electron would be absorbed from a SO_3'' ion which could then lose its second electron, giving sulphate as before, or combine with another singly charged SO_3' ion to give S_2O_6''. Similarly, in a process which involves one electron at a time, HSO_3' ions may be discharged and a molecule of dithionic acid formed by two such neutral radicals.

It has been shown (Table II) that the reduction of tervalent manganese does result in large amounts of dithionate. The *X*-ray evidence shows that the whole of the manganese in manganite and the two forms of Mn_2O_3 is tervalent. Had such high yields not occurred it would be impossible to explain a 95% formation of dithionate in the reduction of MnO_2 by this two-step theory.

Since the proportion of dithionate is nearly independent of conditions, the possibility of complex formation must be examined. The formation of a complex when freshly precipitated ferric hydroxide reacts with sulphurous acid has been established (Seubert and Elten, and Gelis, *loc. cit.*). The first product is a reddish solution of complex ferric sulphite which slowly decomposes with a nearly quantitative yield of dithionate and only a very small amount of sulphate. Manganese could readily form anionic complex sulphites, *viz.*, $[Mn(SO_3)_3]^{2- \text{ or } 3-}$, and since this metal, like iron, is easily reducible to a lower valency stage the complexes could undergo self-oxidation and -reduction to either dithionate or sulphate. This explanation does not require that the proportions of dithionate formed by quadrivalent and tervalent manganese should have a predetermined relationship, but if such complexes are formed *in solution* before reduction occurs it does require that all oxides of one class (*e.g.*, dioxides) should produce the same proportion of dithionate. This is not the case, and therefore it is concluded that the oxidation of sulphurous acid by the oxides and hydroxides examined in this work occurs, not in solution, but on the surface of the oxide. Ferric hydroxide is an exception, dissolution occurring before reduction in that case. The pattern of the surface adsorption may be expected to be determined in large measure by the crystal lattice of the oxide but to be largely independent of the concentration of the solution. This would account for the fact that the proportion of dithionate formed in the reaction is the same over a wide range of concentration for any one variety of oxide.

Reaction on the surface probably has the general mechanism outlined above. An SO_3'' ion, for example, reacting at the surface of manganese dioxide, may be discharged in a single- or a two-step operation and the resultant neutral molecule may form sulphate, or the ion may be partly discharged and be at the same time in close proximity to another ion in a similar state so that the two link up to form a doubly charged S_2O_6'' ion. If this explanation is accepted it is reasonable to suppose that the products will depend largely on the structure of the oxides and the location of the reactive centres. The theory receives strong support from the results which are set out in Table II, for it certainly appears that the dithionate yields from the various oxides fall into groups which can be correlated with the several polymorphic forms of the oxides. It might be supposed that the two polymorphic forms of Mn_2O_3 were respectively $Mn^{III}{}_2O_3$ and $Mn^{II}O,Mn^{IV}O_2$, that they dissolved and formed anionic complexes before reduction, and that these complexes contained Mn^{III} in the one case and Mn^{IV} in the other. The different yields of dithionate could then be ascribed to this difference. It would not be possible on this basis to account for manganite giving still a different proportion of dithionate, for this must yield the same solution as one or the other form of Mn_2O_3.

If the differences are determined by the crystal lattices this difficulty does not arise, for Mn_2O_3,H_2O would naturally have a lattice differing from those of α- and β-Mn_2O_3. It is clear from the *X*-ray evidence in any case that all the manganese in both forms of Mn_2O_3 and in manganite is tervalent.

A surface reaction seems to provide the only mechanism which can explain the different yields of dithionate from the two forms of crystalline MnO_2 and Mn_2O_3. It is also more in keeping with the complete absence of any colour change in the solutions, even in cases where the oxides dissolve rapidly.

It was important for our theory to be sure that dithionate formation never occurred in reductions which must involve a two-electron step. No record of any such case has been found in the literature. We have examined a few such reductions, to confirm the results of earlier workers, and found that sulphate and no dithionate is formed in such cases. Sulphurous acid solutions were oxidised by lead dioxide, mercuric oxide, and mercuric chloride respectively, and in each case only traces of dithionate were obtained which could arise from direct oxidation of the $H_2S_2O_5$. Since the reduction of lead dioxide and mercuric oxide to bivalent lead and metallic mercury respectively must occur in a single stage involving two electrons, the absence of dithionate is explained. Reduction of mercuric chloride to mercurous chlorides is also a two-electron step, since the reaction is $2HgCl_2 \longrightarrow Hg_2Cl_2$, and mercurous chloride is $(Hg\rightarrow Hg)Cl_2$; absence of dithionate could be similarly explained, but reduction of chlorides is peculiar, and even when only a one-electron step is involved no dithionate may be formed (see Part 2).

The figures for dithionate formation from the two forms of MnO_2 (Table II) necessitate the assumption that the reduction of β-MnO_2 by sulphurous acid, if occurring in two stages, must pass through what amounts to the β-Mn_2O_3 phase. Only in this way could the experimental values for dithionate be explained. It is evident, for example, that, even if it is assumed that the reduction β-$Mn^{IV}O_2 \longrightarrow Mn^{III}$ gave a 100% yield of dithionate, a combination of this step with, say, the manganite (64% dithionate) or α-Mn_2O_3 (83% dithionate) step could not give an overall yield of 95—97% of dithionate. It seems likely that reduction of α-MnO_2 would pass likewise through what amounts to the α-Mn_2O_3 phase.

This deduction assumes that the manganese in β-Mn_2O_3 is all tervalent—which is probable from Zachariasen's work (*loc. cit.*). If it were really $Mn^{II}Mn^{IV}O_3$ it could not form the second step in a reduction of β-MnO_2 occurring in two one-electron steps. The second step would have to be taken as some unknown form of Mn_2O_3 other than α-Mn_2O_3 or manganite.

2. OXIDATION BY FERRIC AND CUPRIC SALTS.

Ferric Salts.—Ferric hydroxide and ferric salts occupy rather an important position in connection with the mechanism by which sulphurous acid on oxidation gives dithionate (Bassett and Henry, *loc. cit.*, p. 919). We have confirmed the results obtained by Gélis and by Carpenter (*loc. cit.*) in the reduction of ferric hydroxide by sulphurous acid and have also examined the oxidation of sulphurous acid by ferric salts with some striking results.

Suitable ferric salts are not numerous. We have used the sulphate, nitrate, and chloride in approx. 0·1 equivalent-normal solution (*e.g.*, $FeCl_3/30$ in g. per l.). A solution ten times this strength was also used in the case of the chloride. All the solutions became deep reddish-brown when sulphur dioxide was passed in but this colour faded rapidly.

The ferric sulphate and ferric nitrate solutions gave nearly theoretical yields of dithionate. The 0·1N-ferric chloride converted 53% of the sulphurous acid oxidised into dithionate, although a solution ten times as concentrated gave hardly any dithionate.

0·1N-Nitric acid was found to oxidise sulphurous acid, and 22·8% of the acid oxidised was converted into dithionate. This oxidation by the nitrate had to be allowed for in the ferric nitrate experiment. Addition of hydrochloric acid to the ferric chloride solution greatly reduced the proportion of dithionate which is formed on reduction by sulphurous acid, whereas the effect of added sulphuric acid on the ferric sulphate reaction is quite small.

The experimental results are summarised below.

The behaviour of the sulphate and nitrate solutions is clearly similar to that of the solution of ferric hydroxide in sulphurous acid.

Anions of high electroaffinity such as SO_4'' and NO_3' do not readily form stable complex ions. Complex ferrisulphite anions can accordingly be formed with ease in the sulphate and nitrate solutions and give high yields of dithionate as they undergo oxidation and reduction. The ferrichloride anion $(FeCl_4)'$ is, however, very stable, so that ferrisulphite anions are not so readily formed in the chloride solution.

The following complex ions would appear to be possible in the sulphurous acid solutions prepared from ferric chloride with or without additional chlorions : $[Fe(SO_3)_2]'$; $[FeCl_2(SO_3)]'$; $[FeCl_4]'$. It seems unlikely that any $[Fe(SO_3)_3]'''$ could be present on account of the very low concentration of SO_3'' ions.

Collisions between two $[Fe(SO_3)_2]'$ or one $[Fe(SO_3)_2]'$ ion and either of the other two might give rise to either dithionate or sulphate according to how the two-electron switches occurred.

Collisions between two $[FeCl_2(SO_3)]'$ ions might also yield either dithionate or sulphate, but collisions between $[FeCl_2(SO_3)]'$ and $[FeCl_4]'$ could give only sulphate. Formation of the latter two ions would be favoured by increase in the concentration of any source of chloride ions, even by increase in the concentration of ferric chloride: $2FeCl_3 + H_2SO_3 = H[FeCl_2(SO_3)] + H[FeCl_4]$. It is not surprising therefore to find that although a dilute solution of ferric chloride gives rise to a high proportion of dithionate, a solution of ten times the concentration yields hardly any.

As reduction of the ferric chloride solution takes place all the chloride ions bound in anionic complexes become available for further $(FeCl_4)'$ formation, since the ferrous ion has much less tendency to form complex anions than has the ferric ion. Complex ferrisulphite ions are formed more readily at the commencement of the reduction than later when the proportion of chloride ions increases. Dithionate formation occurs chiefly in the early stages of reduction for this reason.

The effect of added sulphuric acid on the ferric sulphate reaction is to reduce dithionate formation slightly and to slow down the reduction considerably.

The concentration of SO_3'' ions and therefore of ferrisulphite ions is greatly diminished by the addition of sulphuric acid. The collision rate between ferrisulphite ions and their rate of reaction are proportionately depressed. This slowness of reaction under strongly acid conditions appears to render reaction (*a*) more possible than is normally the case, though (*b*) still predominates :

(*a*) $2[Fe(SO_3)_2]' + H_2O = SO_4'' + 2H^{\cdot} + 2Fe^{\cdot\cdot} + 3SO_3''$
(*b*) $2[Fe(SO_3)_2]' = S_2O_6'' + 2Fe^{\cdot\cdot} + 2SO_3''$

The intense colour of the ferrisulphite ions is in full agreement with the well-known effect on colour of having an easily oxidised and an easily reduced group in the same molecule or ion.

Antony and Manasse (*Gazzetta*, 1899, **29**, i, 514) stated that ferric sulphate at 0° gave an 80% yield of dithionate according to the erroneous equation $Fe_2(SO_4)_3 + 3SO_2 + 2H_2O = 2FeS_2O_6 + 2H_2SO_4$ in which half the dithionate formed was supposed to result from combination of SO_2 with sulphate.

EXPERIMENTAL.

Solutions of ammonium ferric alum, sublimed anhydrous ferric chloride, and ferric nitrate, approx. 0·1 equivalent-normal, were saturated with sulphur dioxide and the containers were then tightly corked. All the experiments were carried out at approx. 25°.

The ferric nitrate solution was prepared from a previously analysed solution of ferric chloride which was precipitated with ammonia. The well-washed precipitate was then dissolved by addition of the theoretical amount of a standard nitric acid solution. All the solutions became dark reddish-brown when the sulphur dioxide was passed in. The initial colour was apparently of the same depth with the three solutions to which no additional sulphuric or hydrochloric acid had been added, but in the case of the ferric chloride solution made approximately 0·5N. to free hydrochloric acid it was somewhat paler. After the solutions had become colourless, the sulphur dioxide was displaced by a rapid current of carbon dioxide, complete displacement being confirmed by addition of a drop of 0·1N-iodine.

Analyses of the solutions were carried out by one of the following methods.

(*a*) A small amount of hydrogen peroxide was added to reoxidise the reduced iron (which it does at once). The ferric iron was doubly precipitated by ammonia, and after being well washed was ignited and weighed as Fe_2O_3. The combined filtrates from the ferric hydroxide were acidified with hydrochloric acid and precipitated at 60° barium chloride with constant stirring. To the filtrate and washings from the barium sulphate were added 15 c.c. of concentrated nitric acid for every 100 c.c. of solution, and the mixture was evaporated to dryness on the hot plate. Sufficient barium chloride must be present to combine with all the sulphate resulting from oxidation of dithionate. During the course of the evaporation all ammonium ions are destroyed by the combined effect of the nitric and hydrochloric acids (a great advantage). The residue was treated with about 10 c.c. of concentrated hydrochloric acid (to replace nitrate by chloride). After evaporation of excess of acid, water was added and the barium sulphate, resulting from oxidation of dithionate was determined.

(*b*) The reduced solution was precipitated with ammonia without prior re-oxidation of the iron, and the black hydroxide precipitate was filtered off, washed, redissolved in hydrochloric acid, and reprecipitated with ammonia. This precipitate filtered very slowly and, owing to the appreciable solubility of ferrous hydroxide, a small amount of ferric hydroxide eventually separated from the filtrate and was filtered off separately. The black partly oxidised hydroxide redissolved readily in hydrochloric acid, but there was always a small amount of (probably) γ-Fe_2O_3,H_2O which would not redissolve without use of excessive amounts of hydrochloric acid or undue heating. There was no need for complete dissolution, however, as the object of the second precipitation was only to remove small amounts of strongly adsorbed sulphate and possibly dithionate. From this point the procedure was the same as with method (*a*).

Method (*a*) is greatly preferable but it was necessary to show that the treatment with hydrogen peroxide did not lead to any destruction of dithionate (though dithionate is very resistant to oxidation).

In two otherwise identical experiments with the ferric alum analyses were made by each method. The results were identical within the limits of accuracy.

Oxidation by Ferric Sulphate.—(i) Ammonium ferric alum solution with no added acid (0·1070 g. of Fe_2O_3 per 50 c.c. = 0·0814 equivalent-normal) became colourless after 5 hours. Analysis by method (*a*) showed that 98·5% of the sulphurous acid oxidised gave dithionate. (ii) In a similar experiment, analysis by method (*b*) showed that 99·1% of the sulphurous acid oxidised gave dithionate. (iii) Ammonium ferric alum of the same concentration as above but 0·5N. with respect to free sulphuric acid required *ca.* 12 hours to become colourless; analysis by method (*a*) showed that 94·5% of the total sulphurous acid oxidised gave dithionate.

Oxidation by Ferric Nitrate.—Fe_2O_3 (0·1363 g.) and the equivalent amount of nitric acid (but no additional acid) were made up 50 c.c. (= 0·1023 equivalent-normal). The initial dark reddish-brown colour obtained on passage of sulphur dioxide faded rapidly but there was still a slight pale brownish colour after 6½ hours, probably due to a trace of nitric oxide. The sulphur dioxide was then displaced by a rapid current of carbon dioxide and the solution became colourless. Analysis was by method (*b*). 0·0992 G. of $BaSO_4$ was obtained from the sulphate, and 0·4210 g. from the dithionate formed. Deducting the corresponding amounts resulting from the sulphate and dithionate produced in 6½ hours by 50 c.c. of 0·1N-nitric acid, which are 0·0986 g. of $BaSO_4$ from sulphate and 0·0295 g. from dithionate, we get 0·0006 g. of $BaSO_4$ from sulphate and 0·3915 g. from dithionate as the amounts formed by the ferric iron. Now if 0·1363 g. of Fe_2O_3 gave 100% oxidation to dithionate there would result 0·3982 g. of $BaSO_4$. Thus, the ferric iron in ferric nitrate, at any rate in 0·1 equivalent-normal solution, gives a nearly 100% yield of dithionate.

Oxidation by Ferric Chloride [all but (iv) analysed by method (*b*)].—(i) 0·0798 Equivalent-normal ferric chloride with no additional acid became colourless after 2¼ hours. Of the total sulphurous acid oxidised 53·4% gave dithionate.

(ii) Ferric chloride of the same concentration but 0·1N. with respect to free hydrochloric acid became colourless after 1½ hours; 25·9% of the sulphurous acid oxidised gave dithionate.

(iii) Ferric chloride of the same concentration but 0·5N. with respect to free hydrochloric acid, became colourless in 0·5 hour. Only 2·5% of the sulphurous acid oxidised had formed dithionate.

(iv) Since the effect of added hydrochloric acid was probably due chiefly to the chloride ions the behaviour of approx. equivalent-normal ferric chloride ($FeCl_3/3$ in g. per l.) without added acid was examined. 0·804 Equivalent-normal ferrichloride with no additional acid was used. The initial very dark colour obtained on passage of sulphur dioxide faded very rapidly. After 6 hours the solution was pale, slightly greenish-blue. The sulphur dioxide was then displaced by a rapid current of carbon dioxide, and the solution lost most of its greenish tinge but remained rather greener than a solution of ferrous ammonium sulphate of corresponding concentration, in accord with the fact that the sulphate and dithionate formed showed that only 95·8% of the ferric salt had been reduced. Complete reduction takes a long time in concentrated solutions. Analysis by method (*a*) showed that only 3·0% of the total sulphur dioxide oxidised had yielded dithionate.

Cupric Salts.—Cupric sulphate and nitrate are not reduced by sulphurous acid, but in solutions containing a large excess of alkali sulphite where cuprisulphite anions probably exist reduction to the cuprous condition does occur and about 70% of the sulphite oxidised is converted into dithionate (Baubigny, *Ann. Chim. Phys.*, 1910, **20**, 12; *Compt. rend.*, 1912, **154**, 701). Cupric chloride is reduced by sulphurous acid, and cuprous chloride is precipitated. We found that the oxidation product is sulphate with a very small proportion of dithionate. In this case also, a larger proportion of dithionate is obtained from a 0·1 equivalent-normal cupric chloride than from one of ten times the strength. The reaction evidently takes a course similar to that followed in the case of ferric chloride.

EXPERIMENTAL.

The experiments were carried out at approx. 25°.

Complete reduction of the cupric salt had not occurred in either case. After displacement of sulphur dioxide the copper was precipitated cold with a small excess of potassium hydroxide. The filtrate and washings were acidified with hydrochloric acid, the sulphate precipitated at 60°, and the filtrate from the barium sulphate oxidised with nitric acid as in other experiments.

(i) 0·1 *Equivalent-normal Cupric Chloride.*—The pale blue solution took on a slight greenish tinge on saturation with sulphur dioxide. The first slight separation of crystals of cuprous chloride occurred after 20 hours. A considerable amount had separated after another 24 hours but was beginning to become discoloured owing to disproportionation $2CuCl \rightleftharpoons Cu + CuCl_2$. The sulphur dioxide was then displaced, and the solution lost its greenish tinge and became pale blue. The precipitated cuprous chloride was filtered off, and the filtrate analysed. The colour of the precipitate obtained with potassium hydroxide indicated that both cupric and cuprous copper must be present. 1·4% of the total sulphur dioxide oxidised had yielded dithionate, and the sulphate plus dithionate obtained corresponded to reduction of 54·4% of the original cupric chloride.

(ii) 1·0 *Equivalent-normal Cupric Chloride.*—The solution became fairly dark yellowish-green on passage of sulphur dioxide. Separation of cuprous chloride began almost at once and a large amount had separated after 19 hours, the solution being still yellowish-green. The precipitate remained quite white. The sulphur dioxide was then displaced, the cuprous chloride removed by filtration, and the solution analysed as above. 81·4% of the original cupric chloride had been reduced and only 0·21% of the sulphur dioxide oxidised had yielded dithionate.

3. THE INFLUENCE OF DISSOLVED SALTS ON THE OXIDATION OF SULPHUROUS ACID SOLUTION BY FREE OXYGEN.

Oxidation of sulphurous acid solution by free oxygen yields sulphuric and dithionic acids. The latter may amount to several per cent. of the total sulphur dioxide oxidised.

The rate of the oxidation is considerably affected by the salts of certain metals, and the relative amounts of sulphuric and dithionic acids may be changed thereby. For example, manganese sulphate greatly increases the quantity of sulphurous acid oxidised, but the increase is entirely in favour of sulphate formation and the amount of dithionate obtained is negligible.

It is generally assumed, by analogy with the oxidation of sodium sulphite solution, that this reaction has a chain mechanism and that the presence of a salt may help to initiate more chains. The effect of the salt on the dithionate formation has received practically no attention.

In 1847 Jacquelain (*Ann. Chim. Phys.*, 1847, [iii], **21**, 110) stated erroneously that sulphurous acid solution was slowly oxidised by air to dithionic acid which was then oxidised to sulphuric acid. The effect of dissolved salts on the sulphurous acid oxidation was first studied by L. Meyer (*Ber.*, 1887, **20**, 3058) who passed a mixture of sulphur dioxide and oxygen through boiling solutions of the salts and estimated the sulphate formed after a definite time. He did not test for dithionate but observed that the oxidation was accelerated considerably by salts of manganese or copper. He listed a number of salts in order of their influence on the reaction. Sulphates and chlorides of Mn, Cu, Fe, and Co, and the sulphates of Ni, Zn, Cd, Mg, cuprous chloride, copper oxide, and even metallic copper had an effect, but thallium and potassium sulphates and sulphuric acid were without effect.

Bachmann (*Ber.*, 1888, **21**, 175) showed that potassium, sodium, and ammonium sulphites were oxidised at similar rates and more quickly than the corresponding hydrogen sulphites or sulphurous acid. The oxidation of pure sodium sulphite solution is slow, according to Titoff (*Z. physikal. Chem.*, 1930, **45**, 641), but may be accelerated by traces of copper, copper sulphate having a noticeable effect in molar concentrations as low as 10^{-13}. The reaction is also retarded by many substances and Bigelow (*ibid.*, 1898, **26**, 493) and Young (*Amer. Chem. J.*, 1901, **23**, 119) examined these. Organic substances like benzyl alcohol were powerful retarding agents and salts such as potassium cyanide, ammonium chloride, and sodium acetate had some effect. In each case Young found the effect greater in alkaline than in neutral solutions, and it appeared from work by Lumière (*Bull. Soc. chim.*, 1950, **33**, 444) that the reactions were not retarded indefinitely, oxidation setting in after a prolonged induction period.

Catalytic acceleration and retardation are closely associated phenomena, and Moureu and Dufraisse have published since 1923 (in the *Compt. rend.*) a large number of papers on the subject. Thus Dufraisse and Horclois (*ibid.*, 1930, **191**, 1126) found that ammonium ferrous sulphate (1%) accelerated the oxidation of a 10% solution of sodium sulphite in water made slightly acid, while the ferric acetylacetone complex retarded it. Ferric hydroxide retarded the oxidation in feebly alkaline solution. Reactions with cobalt salts showed similar effects (Dufraisse and Nakal, *ibid.*, 1932, **194**, 880).

Autoxidation of neutral sodium sulphite solution was shown by Bäckstrom (*J. Amer. Chem. Soc.*, 1927, **49**, 1460) to be a chain reaction. He found, in the photochemical reaction, that each light quantum absorbed caused a great number of molecules to react and since the thermal and photochemical reactions were similarly affected by inhibitors he concluded that the mechanisms of the two reactions must also be similar. The actual mechanism of this oxidation chain is still in doubt, but Franck and Haber (*Sitzungsber. Preuss, Akad. Wiss. Berlin*, 1931, 250) treated it as a particular case of their general theory of homogeneous catalysis in aqueous solutions, in which the essential primary process is the " univalent " oxidation of substrate by the catalyst to an unsaturated radical, R_1, which undergoes a second univalent oxidation to reaction product whereby a second radical, R_2, is formed having the properties of a univalent oxidiser. R_2 effects univalent oxidation of substrate with regeneration of R_1. The catalyst is oxidised back to normal by some process and starts a new chain. In the sodium sulphite oxidation the chain is usually started by a heavy-metal ion accidentally present, thus :

$$\left.\begin{aligned} SO_3'' + Cu^{\cdot\cdot} &= SO_3' + Cu^{\cdot} \\ SO_3' + H^{\cdot} &= HSO_3\ [\equiv R_1] \\ HSO_3 + O_2 + H_2O + SO_3'' &= 2SO_4'' + 2H^{\cdot} + OH\ [\equiv R_2] \\ SO_3'' + OH + H^{\cdot} &= HSO_3 + OH' \end{aligned}\right\} \quad \text{I}a$$

The formation of dithionate in such reactions is attributed to dimerisation of HSO_3 or SO_3'. This unknown acid or its anion was postulated as the chain-starting radical since dithionic acid was detected when these reactions took place in the absence of oxygen. Bassett and Henry (*J.*, 1935, 919) were unable to confirm the formation of dithionate either in the oxidation of dissolved sodium sulphite by free oxygen or in the photochemical decomposition of sodium hydrogen sulphite solution in the absence of free oxygen.

The oxidation of sulphite solution proceeded slowly in strongly acid conditions according to Albu and Goldfinger (*Z. physikal. Chem.*, 1932, **16**, 338), and Haber and Wansborough-Jones (*ibid.*, **18**, p. 103) attributed this to a reduction in the number of sulphite ions in acid solution, it being assumed that the sulphite ions are the most readily oxidised.

Hoather and Goodeve (*Trans. Faraday Soc.*, 1934, **30**, 1149) found that the rate of oxidation of sulphurous acid catalysed by manganese or ferrous sulphate was depressed by the addition of sulphuric acid although the acid formed by the reaction did not have a marked effect, and Bassett and Henry (*loc. cit.*) showed that the relative amounts of dithionate and sulphate depended on both the acidity and the sulphur dioxide concentration.

Bigelow (*loc. cit.*) recorded that the rate of oxidation of a sodium sulphite solution was proportional to the quantity of air passing through the solution ; Miyamoto and Kaya (*Bull. Chem. Soc. Japan*, 1930, **5**, 123) confirmed this for fairly strong solutions, and in a detailed study of the point (*ibid.*, 1931, **6**, 264) they found that the rate of absorption increased as the concentration of the sulphite solution increased to 0·35N., remained constant between 0·35N. and 0·75N., and then declined. They concluded that in the interval of constant absorption velocity there were enough sulphite molecules in the surface to react with all the oxygen molecules entering that surface.

EXPERIMENTAL.

Five Dreschel bottles of similar size were connected in series. The first contained 75 c.c. of distilled water and the other four 75 c.c. each of different concentrations of the salt solution under investigation. A current of washed sulphur dioxide was passed through the bottles, immersed in a water thermostat at 25°, until all the solutions were saturated with sulphur dioxide at atmospheric pressure.

A sulphur dioxide–oxygen mixture, issuing from a suitably adjusted flowmeter, was then passed through the five bottles, usually for 15—17 hours. The stream of mixed gases was then replaced by one of carbon dioxide until the excess of sulphur dioxide was displaced (complete freedom being checked with iodine before the solutions were analysed).

The influence of the relative partial pressures of oxygen and sulphur dioxide on the rate of oxidation is shown by the following results.

With the flowmeter adjusted as in all the experiments listed in Tables III—VII and delivering 10 c.c. of oxygen and 23 c.c. of sulphur dioxide per minute, the total oxidation in the first bottle of the first series in Table III was equivalent to 0·08 g. of barium sulphate per hour, which corresponded to only 0·7% of the oxygen passing during this time.

The sulphur dioxide and oxygen jets in the flowmeter were then interchanged, so that the rates of flow were reversed. The total oxidation was increased by more than 40% but no significant change in the dithionate : sulphate ratio was observed. It follows that major variations of partial pressures must be avoided if reproducible results are to be obtained, but small accidental variations are not likely to affect seriously either the rate of oxidation or the proportion of dithionate formed. The necessity for good temperature control is shown by Table III (*c*). All the experiments recorded in Tables III—VII were made at 25°.

When the sulphur dioxide–oxygen mixture was passed through five bottles in series which originally contained water only, saturated with sulphur dioxide at atmospheric pressure, the results given in Tables III (*a*) and (*b*) were obtained. The proportion oxidised to dithionate in the several bottles was constant within the limits of error of the determinations but there was a significant drop in the total amount oxidised as one went from the first to the last bottle. Since a more than four-fold increase in the partial-pressure ratio $O_2 : SO_2$ only increased the rate of oxidation by 40%, it is not likely that a 0·7% decrease in the amount of oxygen passing would cause a fall of more than 2% in the amount oxidised in the second bottle compared with the first, and some other explanation for the marked decrease from bottle to bottle must be sought. The following seems to be the most likely.

Initially all the bottles contain sulphurous acid saturated with sulphur dioxide at approx. atmospheric pressure. When the oxygen–sulphur dioxide mixture is passed through the bottles, sulphur dioxide is gradually displaced from the solutions until the concentration is reduced to that appropriate to a sulphur dioxide partial pressure of only 23/33 of an atmosphere. During this process the sulphur dioxide displaced is passed on from bottle to bottle so that in effect the solution in each successive bottle undergoes oxidation at a considerably lower oxygen partial pressure than can be accounted for by the small amount of oxygen used up by the oxidation occurring in each bottle. Oxidation at this lower oxygen pressure persists for a larger fraction of the whole period with each successive bottle. In spite of this drawback, the method of experimentation still seemed the most convenient and satisfactory for the object we had in view, as the above effect could easily be allowed for.

The time for each experiment varied somewhat in different experiments, and hence also the total amount of oxidation which occurred in the first bottle.

The amount of barium sulphate which would have been obtained from each bottle, had it only contained sulphurous acid without an added salt, was then calculated by simple proportion from the weight obtained from the first bottle in any series and from the various bottles of Table III (*a*) and (*b*). The difference between the figures so calculated and the experimental figures shown in the third column of the various tables gives the increase or decrease in the amount of oxidation due to the dissolved salt. It is these differences which are given, as percentages, in column 4.

In solutions of sulphates stronger than 0·05M. a large proportion of the total sulphate found by analysis is due to the original salt. This disadvantage led to the use of chlorides, since it was expected that the catalytic effect of a salt would be due entirely to the cation. This expectation was not entirely fulfilled, and both sulphate and chloride were investigated in some cases.

Interference of a series by the salt of a preceding series was not detected. The bottle used for the blank determination (*i.e.*, the first bottle) never contained a salt solution and all the bottles were rinsed with hot distilled water before each series. No organic liquid was used. A strong poisoning effect was noted on one occasion when sulphurous acid without any added salt was being oxidised, and it persisted until traced to some new rubber tubing connecting various parts of the flowmeter. It was presumed that an organic accelerator or antioxidant present in the rubber was responsible. The tubing was replaced by some which had been in use previously and glass-to-glass joints made wherever possible. The poisoning effect disappeared immediately.

Analyses of Solutions after Oxidation.—The solution after oxidation was freed from sulphur dioxide and was made up to 200 c.c. Sulphate and dithionate were determined in separate portions essentially as described by Bassett and Henry (*loc. cit.*, p. 923). The portion to be analysed for dithionate was treated in the cold with barium hydroxide solution in slight excess, and the precipitate of barium sulphate and metal hydroxide filtered off after settling overnight. Dithionate determinations carried out in this way are usually slightly high on account of barium nitrate occluded by the sulphate. A series of determinations made on pure $Na_2S_2O_6,2H_2O$ showed that the mean value was 0·5% high and that the probable error was ±3%. This appears as an error of only ± 0·12% when the dithionate itself only amounts to 4% of the total sulphur dioxide oxidised (as in so many of the experiments below). This is in fair agreement with the corresponding error deduced from the variation of dithionate in the results of the series shown in Tables III (*a*) and (*b*).

Experimental Results.—These are shown in the Tables. " Normality " in Tables IV—VII refers to equivalent-normality, *i.e.*, NaCl, $NiCl_2/2$, $FeCl_3/3$, etc., in g./l.

TABLE III.

Sulphurous acid solutions saturated with SO_2 *at* 25°.

(*a*) *First series.*

Position in series.	Total SO_2 oxidised ($BaSO_4$, g.).	Change (%) of total oxidation in the series.	SO_2 (%) oxidised to S_2O_6''.
1st	1·2485	—	4·07
2nd	1·2208	−2·2	3·88
3rd	1·1623	−6·9	3·95
4th	1·0951	−12·3	4·24

(*b*) *Second series.*

Position in series.	Total SO_2 oxidised ($BaSO_4$, g.).	Change (%) of total oxidation in the series.	SO_2 (%) oxidised to S_2O_6''.
1st	1·2304	—	3·83
2nd	1·2024	−2·3	3·84
3rd	1·1400	−7·4	3·90
4th	1·0496	−14·7	4·07
5th	1·0064	−18·2	4·21

Probable error in the determination of the percentage dithionate formed, calc. from the variation from the mean value : (*a*) ±0·16, (*b*) ±0·15%.

(*c*) *Sulphurous acid solutions saturated with* SO_2 *and oxidised at various temperatures.*

Temp.	0	15	25	35—40
SO_2 (%) oxidised to S_2O_6''	4·8	4·6	3·7	2·5

TABLE IV.

Solutions containing hydrochloric acid.

Position in series.	Normality of HCl.	Total SO_2 oxidised ($BaSO_4$, g.).	Change (%) of total oxidation.*	$BaSO_4$ (g.) from S_2O_6''.	SO_2 (%) oxidised to S_2O_6''.
1st	0	2·3607	—	0·0938	4·0
2nd	0·01	2·2730	− 1·5	0·0895	3·9
3rd	0·10	1·9882	− 9·4	0·0777	3·9
4th	0·50	0·9952	−51·3	0·0268	2·7
5th	1·00	0·2904	−85·0	0·0069	2·4

* Values given in this column and in the corresponding columns of Table V are corrected for the positions of the bottles in the series as explained on p.1552.

TABLE V..

Solutions containing sodium chloride.

Position in series.	Normality of salt solution.	Total SO_2 oxidised ($BaSO_4$, g.).	Change (%) in total oxidation.	$BaSO_4$ (g.) from S_2O_6''.	SO_2 (%) oxidised to S_2O_6''.
(*a*) *First series.*					
1st	0	1·7624	—	0·0729	4·1
3rd	0·02	1·8892	15·5	0·0797	4·2
4th	0·07	1·6999	10·4	0·0779	4·6
2nd	0·50	1·4635	−15·0	0·0840	5·8
(*b*) *Second series.*					
1st	0	1·5110	—	0·0675	4·5
2nd	0·50	1·1681	−20·9	0·0676	5·8
3rd	1·00	0·8290	−40·9	0·0510	6·2
4th	2·00	0·5905	−54·8	0·0425	7·2
5th	0	1·2142	−1·8	0·0527	4·3
Solutions containing ammonium salts.					
(*a*) *Ammonium chloride.*					
1st	0	1·8810	—	0·0820	4·4
2nd	0·1	1·8455	0·4	0·0875	4·7
4th	0·5	1·3098	−19·4	0·0778	5·9
3rd	1·0	1·2810	−26·7	0·0810	6·3
5th	2·0	0·9190	−40·3	0·0595	6·5
(*b*) *Ammonium molybdate.*					
1st	0	1·3216	—	0·0600	4·5
2nd	0·001	1·4020	8·5	0·0648	4·6
3rd	0·01	1·0615	−13·4	0·0475	4·5
4th	0·10	0·8131	−28·8	0·0411	5·1
5th	1·0	0·7171	−33·7	0·0541	7·5
Solutions containing magnesium sulphate.					
1st	0	1·6039	—	0·0709	4·4
2nd	0·03	1·9301	23·1	0·0879	4·6
4th	0·08	1·4355	3·5	0·0655	4·6
3rd	0·23	1·3800	−7·3	0·0675	4·9
5th	0·43	1·0810	−17·6	0·0544	5·0
Solutions containing zinc sulphate.					
1st	0	1·5324	—	0·0614	4·0
2nd	0·011	1·6508	9·6	0·0685	4·2
4th	0·033	1·5163	14·3	0·0658	4·3
3rd	0·074	1·4199	−2·1	0·0621	4·4
5th	0·156	1·1981	−4·5	0·0566	4·7
Solutions containing aluminium sulphate.					
1st	0	1·5132	—	0·0669	4·4
2nd	0·022	1·7765	20·2	0·0695	3·9
3rd	0·084	1·4381	2·3	0·0664	4·6
4th	0·23	1·3278	1·5	0·0431	3·2
5th	0·50	0·9020	−27·1	0·0388	4·3

TABLE V.—*continued.*

Position in series.	Normality of salt solution.	Total SO_2 oxidised ($BaSO_4$, g.).	Change (%) in total oxidation.	$BaSO_4$ (g.) from S_2O_6''.	SO_2 (%) oxidised to S_2O_6''.
(*a*) *Solutions containing manganese sulphate.*					
1st	0	0·2474	—	0·0170	6·9 *
2nd	0·011	0·6827	182	0·0115	1·7
3rd	0·103	1·5779	587	0·0019	0·1
4th	0·353	1·7874	735	0·0026	0·1
(*b*) *Solutions containing manganese chloride.*					
1st	0	1·6175	—	0·0697	4·3
2nd	0·01	2·4055	52·2	0·0100	0·4
4th	0·05	4·2304	202	0·0057	0·1
5th	0·10	5·2779	299	0·0054	0·1
3rd	0·20	6·5262	325	0·0050	0·1
(*c*) *Solutions containing manganese chloride* (*more concentrated*).					
1st	0	1·1022	—	0·0452	4·1
3rd	0·5	4·8938	378	0·0038	0·1
2nd	1·0	4·8355	349	0·0045	0·1
5th	2·8	0·5759	−36·2	0·0041	0·7
4th	4·0	0·3029	−68·2	0·0067	2·2
(*a*) *Solutions containing cobalt sulphate.*					
1st	0	1·1778	—	0·0461	3·9
2nd	0·007	1·5315	33·1	0·0430	2·8
4th	0·03	1·4396	41·2	0·0396	2·8
3rd	0·10	1·5393	40·7	0·0328	2·1
(*b*) *Solutions containing cobalt chloride.*					
1st	0	1·1538	—	0·0510	4·4
2nd	0·007	1·3642	20·9	0·0520	3·8
3rd	0·032	1·1518	7·5	0·0463	4·0
5th	0·054	1·0182	7·8	0·0414	4·1
4th	0·097	1·1103	11·2	0·0438	3·9
(*a*) *Solutions containing nickel sulphate.*					
1st	0	1·4531	—	0·0628	4·3
2nd	0·006	1·8908	33·2	0·0408 *	2·2 *
5th	0·021	1·5173	28·3	0·0373	2·5
3rd	0·070	1·7796	31·9	0·0316	1·8
4th	0·107	1·5851	26·1	0·0381	2·4
(*b*) *Solutions containing nickel chloride.*					
1st	0	1·1661	—	0·0525	4·5
2nd	0·007	1·1817	3·7	0·0501	4·2
3rd	0·027	1·2183	12·5	0·0492	4·0
4th	0·061	1·0962	8·6	0·0426	3·9
5th	0·10	0·8889	−6·8	0·0348	3·9
(*a*) *Solutions containing ammonium ferrous sulphate.*					
1st	0	1·5953	—	0·0690	4·3
2nd	0·006	1·8248	17·1	0·0263	1·4
3rd	0·028	1·6274	9·9	0·0288	1·8
4th	0·08	1·5068	9·2	0·0286	1·9
5th	0·14	1·1940	−8·5	0·0533	4·5
(*b*) *Solutions containing ferrous sulphate.*					
1st	0	1·6806	—	0·0694	4·1
2nd	0·001	1·7138	4·3	0·0480	2·8
3rd	0·01	1·8531	18·7	0·0299	1·6
4th	0·10	1·7688	21·6	0·0633	3·6
5th	1·00	1·0174	−26·0	0·0910	8·9

* Note: the gas flowmeter was not used in this series. The high proportion of dithionate is probably due to the fact that the experiment was stopped at an early stage so that oxidation had occurred in more concentrated solutions than usual.

* Low result due to loss during evaporation with nitric acid.

Table VI.

Position in series.	Normality of salt solution.	Total SO_2 oxidised ($BaSO_4$, g.).	Change (%) in total oxidation.	$BaSO_4$ (g.) equiv. to oxidation of SO_2 by single reduction of $Fe^{3+} \longrightarrow Fe^{2+}$.		$BaSO_4$ (g.) from S_2O_6''.	SO_2 (%) oxidised to S_2O_6''.
(*a*) *Solutions containing ferric sulphate.*							
1st	0	1·468	—	0·000	Double these amounts for dithionate formation	0·0535	3·6
2nd	0·015	1·580	10·1	0·044		0·0571	3·6
3rd	0·15	1·885	38·3	0·437		0·5718	30·3
4th	1·50	5·554	337	4·376		4·6210	83·2
(*b*) *Solutions containing ferric chloride.*							
1st	0	1·580	—	0·000		0·0560	3·5
2nd	0·02	2·538	64·4	0·058		0·0533	2·1
3rd	0·21	3·004	106	0·613		0·0443	1·5
4th	2·86	8·024	487	8·344		0·0179	0·2

Table VII.

Position in series.	Normality of salt solution.	Total SO_2 oxidised ($BaSO_4$, g.)	Change (%) in total oxidation.	$BaSO_4$ (g.) from S_2O_6''.	SO_2 (%) oxidised to S_2O_6''.
(*a*) *Solutions containing cupric sulphate.*					
1st	0	1·1931	—	0·0642	5·4
3rd	0·011	0·7216	−34·9	0·0244	3·4
2nd	0·028	0·8549	−26·7	0·0261	3·1
5th	0·087	1·1539	18·2	0·0191	1·7
4th	0·190	1·7132	66·0	0·0144	0·8
(*b*) *Solutions containing cupric chloride.*		1*st series.*			
1st	0	2·0012	—	0·0612	3·1
4th	N/20,000	1·4644	−15·4	0·0676	4·6
3rd	N/2,000	1·2158	−34·6	0·0710	5·8
2nd	N/200	0·5402	−72·4	0·0402	7·4

Position in series.	Normality of salt solution.	Total SO_2 oxidised ($BaSO_4$, g.).	Change (%) in total oxidation.	$BaSO_4$ (g.) equiv. to oxidation of SO_2 by single reduction of $Cu^{2+} \longrightarrow Cu^{+}$.	$BaSO_4$ (g.) from S_2O_6''.	SO_2 (%) oxidised to S_2O_6''.
(*c*) *Solutions containing cupric chloride.*			2*nd series.*			
1st	0	1·7493	—	0·0	0·0742	4·2
2nd	0·011	0·5659	−67·0	0·048	0·0256	4·5
3rd	0·032	0·9263	−43·4	0·140	0·0221	2·4
4th	0·069	1·5538	1·0	0·302	0·0196	1·3
5th	0·188	2·0151	36·0	0·822	0·0261	1·3
(*d*) *Solutions containing cupric chloride.*			3*rd series.*			
1st	0	2·4368	—	0·0	0·1037	4·3
2nd	0·1	1·9619	−17·6	0·438	0·0339	1·7
3rd	1·0	7·6805	244	4·376	0·0293	0·4
4th	2·0	12·5335	495	8·752	0·0283	0·2

Discussion.

Tables III—VII show that the electrolytes examined can be divided into several groups according to the influence they exert on the oxidation of sulphurous acid by molecular oxygen.

(i) Hydrochloric acid retards the oxidation and lowers the dithionate : sulphate ratio.

(ii) Salts of Na, NH_4, Mg, Zn, and Al seem to accelerate the oxidation a little at low salt concentrations, but they definitely retard the reaction when the concentration is much above 0·05N. The proportion of dithionate either is unaffected or increases somewhat at higher salt concentrations, more particularly with sodium and ammonium salts.

(iii) The total oxidation is enormously increased in presence of manganese salts. An increase is found with salt concentrations as low as N/10,000 (as shown by a few exploratory tests not recorded in the Tables) and rapidly becomes greater as the salt concentration increases. It eventually falls off at salt concentrations above about 2N.; manganese sulphate is a much more potent catalyst than the chloride. The increased oxidation is entirely caused by sulphate formation. Dithionate is, to a great extent, suppressed, the absolute amount which is formed being reduced to about a tenth of that obtained in absence of the manganese salt.

(iv) Cobalt and nickel sulphates appear to act similarly to manganese salts; they cause a considerable though much smaller increase in the rate of sulphate formation. Unlike manganese salts they do not greatly reduce the absolute amount of dithionate formed. The increased oxidation brought about by cobalt and nickel chlorides is much smaller, being of the same order as that caused by Na, NH_4, Mg, Zn, and Al salts.

(v) Ferrous sulphate appears to have a small catalytic activity. There is some evidence that a part of this is caused by oxidation to the ferric salt by molecular oxygen, followed by reduction of the ferric salt.

(vi) Ferric and cupric salts appear to act both catalytically and as direct oxidants. Very low concentrations of copper salts cause a marked *retardation* of the oxidation.

The chain reaction mechanism put forward by Franck and Haber (*loc. cit.*) for the oxidation of sodium sulphite by gaseous oxygen, in which the chains are initiated by small quantities of heavy-metal ions such as copper, may well play an important part in the reaction but appears to be inadequate by itself to explain all the observations on the oxidation of concentrated sulphurous acid solutions in presence of different salts. Very low concentrations of copper salts (*e.g.*, M/40,000) are found to *retard* the oxidation and, although manganese salts in small concentration do accelerate the oxidation, the chain mechanism does not explain how the formation of dithionate is suppressed. If dithionate resulted from dimersation of the hypothetical HSO_3, as in Franck and Haber's chain mechanism, its amount should increase with an increase in the number of chains, while the amount of dithionate resulting from an independent mechanism (*e.g.*, oxidation of $H_2S_2O_5$) should remain independent of the manganese concentration.

The fact that the uncatalysed atmospheric oxidation of alkali sulphite solutions is more rapid than that of sulphurous acid solutions of equivalent concentrations (Bachmann, *loc. cit.*), taken in conjunction with the effect of acid on the oxidation of sulphurous acid (Table II), makes it probable that it is ions which are oxidised rather than un-ionised molecules. These ions may be SO_3'', HSO_3', S_2O_5'', or HS_2O_5'. They may be supposed to have some tendency to add an oxygen molecule by co-ordination to a sulphur atom. These complexes could take part in the Franck–Haber chain mechanism even better than the separate ions and oxygen molecules. Sulphate could result from $(O_2 \rightarrow SO_3)''$ or $(O_2 \rightarrow SO_3H)'$, and dithionate from $(O_2 \rightarrow S_2O_5)''$ or $(O_2 \rightarrow S_2O_5H)'$. The equations for two such reactions could be :

$$\left.\begin{array}{ll} & \left.\begin{array}{r} HSO_3 + (O_2 \rightarrow SO_3)'' + H_2O = 2SO_4'' + 2H^{\cdot} + OH \\ SO_3'' + OH + H^{\cdot} = HSO_3 + OH' \end{array}\right\} \\ \text{and} & \left.\begin{array}{r} HSO_3 + (O_2 \rightarrow HS_2O_5)' + H_2O = HSO_4' + HS_2O_6' + H^{\cdot} + OH \\ SO_3'' + OH + H^{\cdot} = HSO_3 + OH' \end{array}\right\} \end{array}\right\} \text{I}b$$

Added acid, in so far as it shifted the reactions

$$H^{\cdot} + SO_3'' \longrightarrow HSO_3' \xrightarrow{+H^{\cdot}} H_2SO_3 \xrightarrow{+SO_2} H_2S_2O_5 \longrightarrow H_2O + 2SO_2$$
$$HSO_3' + SO_2 \longrightarrow HS_2O_5'$$

from left to right would tend to increase the proportion of dithionate to sulphate formed on oxidation, but since the SO_3'' would almost disappear after the addition of very little acid and since the reaction $HSO_3' + SO_2 \rightleftharpoons HS_2O_5'$ is virtually independent of the acidity this effect would not be easily detected with sulphurous acid solutions. Total sulphur dioxide solubility will decrease at higher acidities, and the rate of formation of both sulphate and dithionate will tend to decrease in consequence but not necessarily at the same rate. The experimental results show that dithionate formation falls off more quickly than that of sulphate.

In addition to reactions of the Franck–Haber type it would appear possible for reactions such as the following to occur independently, though more slowly.

$$\left.\begin{array}{ll} (a) & (O_2 \rightarrow SO_3H)' + HSO_3' = 2HSO_4' \\ (b) & (O_2 \rightarrow S_2O_5H)' + HS_2O_5' = 2HS_2O_6' \end{array}\right\} \text{II}$$

The relatively small increase in the rate of oxidation which is brought about by the presence of salts of Na, NH_4, Mg, Zn, and Al in low concentration can probably be accounted for satisfactorily by the normal " neutral salt effect." This should cause an *increase* in the rate of reaction between *similarly charged ions* such as those involved in reactions II but would not be expected to affect reactions of the Franck–Haber type.

Dithionate formation is little affected by low concentrations of these salts. The diminished rate of oxdiation with higher concentrations of the same salts is presumably due chiefly to decreased solubility of oxygen.

Manganous salts have a far greater catalytic effect on the sulphurous acid oxidation than have any other salts examined. The rate of sulphate formation is enormously increased, while dithionate formation is almost completely suppressed.

It is suggested that the catalytic effect of $Mn^{\cdot\cdot}$ can be explained by supposing that a $[Mn(SO_3)_2]''$ or similar ion adds an oxygen molecule very readily both by direct addition and by depriving $(O_2\!\rightarrow\!SO_3)''$ and similar complexes of their O_2, thus :

$$(O_2\!\rightarrow\!SO_3)'' + [Mn(SO_3)_2]'' = (SO_3)'' + [O_2\!\rightarrow\!Mn(SO_3)_2]''$$

The new complex undergoes rapid rearrangement

$$[O_2\!\rightarrow\!Mn(SO_3)_2]'' = [Mn(SO_4)_2]'' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{III}$$

but since ions of low electro-affinity such as $(SO_3)''$ will tend to replace those of high electro-affinity any complex sulphate ion such as the above would break up and fresh sulphite complexes would be formed. The effect of the manganese is thus to replace the chain reactions I*a* and I*b*, and reactions such as those shown in equation II(*a*) and II(*b*) by an entirely different mechanism III. This will yield practically nothing but sulphate, because complexes containing $(S_2O_5)''$ ions will have little tendency to be formed, both on account of the high electro-affinity of $(S_2O_5)''$ in comparison with $(SO_3)''$ and for steric reasons.

The catalytic effect of cobalt, nickel, and ferrous sulphates is much less than that of manganese sulphate, but more marked than that of magnesium or zinc sulphates. Dithionate formation is reduced but not almost suppressed as with manganese. The results observed are consistent with the view that the increased oxidation brought about by these three salts is partly caused by the " neutral salt effect " and partly by a true catalysis involving complex anions containing added oxygen of a type similar to the manganese complex. The total oxidation in the presence of cobaltous, nickel, or ferrous salts would thus involve three quite different mechanisms, of the types illustrated by equations I*a*, I*b*, II, and III.

The presence of chloride ions interferes with the formation of the sulphite complexes because of the stability of complex chloride ions (see Part 2). It is for this reason that the catalytic activity of cobalt and nickel chlorides is practically nil, while that of even manganese chloride is only from one-third to one-half of that of the sulphate at similar concentrations.

Manganese chloride is as active in suppressing dithionate formation as is manganese sulphate. This suggests that $(MnCl_4)''$ ions are just as able to deprive $[O_2\!\rightarrow\!SO_3]''$ complexes of their oxygen molecule to form $[O_2\!\rightarrow\!MnCl_4]''$ as are the $[Mn(SO_3)_2]''$ ions to form $[O_2\!\rightarrow\!Mn(SO_3)_2]''$. The result is that, while the whole of the manganese present is effective in suppressing the original mechanisms of types I*a* and I*b* with their dithionate formation, only from one-third to one-half carries on the oxidation by the new mechanism. There will be some equilibrium between $[O_2\!\rightarrow\!MnCl_4]''$ and $[O_2\!\rightarrow\!Mn(SO_3)_2]''$ complexes, and the catalytic effects suggest that the concentration of the chloride complexes is about twice that of the sulphite complexes. The metal sulphates are so much less soluble than the chlorides that only sulphate solutions of comparatively low concentrations can be examined for catalytic activity. When the salt concentrations are high enough—even with manganese salts—oxidation of sulphurous acid falls off greatly owing to decreased solubility of oxygen or sulphur dioxide or both.

If the strength of the $O_2\!\rightarrow$metal link is too great, then, while the complex oxygen–(metal sulphite) ions will be formed, their stability may be such that further reaction may be slow. This appears to be the situation with ferrous sulphate (Table V). The results suggest that the salt increases the rate of reaction more than would be expected from the mere neutral salt effect, while the decrease in dithionate formation at low salt concentrations suggests a marked change in the reaction mechanism although at higher salt concentrations there are indications of a large *increase* in dithionate formation. Now the ferrous ion has itself a marked tendency to be oxidised, so that it is probable that O_2 would form the $[O_2\!\rightarrow\!Fe(SO_3)_2]''$ complex even more readily than that containing manganese. This would prevent the original I*a* and I*b* mechanisms. Owing to the reluctance of the iron atom to part with the oxygen the subsequent reaction is little faster than the oxidation which occurred in absence of the iron but its mechanism is quite different. It appears as if two quite different reactions occurred, *viz.* :

(i) some of the $[O_2\rightarrow Fe(SO_3)_2]''$ reacts as does the corresponding manganese complex to give $[Fe(SO_4)_2]''$ which then breaks up to give SO_4'';

(ii) some of the complex reacts in such a way that the iron is oxidised to the ferric state. The reaction might be :

$$2[O_2\rightarrow Fe(SO_3)_2]'' + 2H^{\cdot} = 2Fe^{\cdot\cdot\cdot} + H_2O + 3(SO_4)'' + (SO_3)''$$

The ferric iron would be converted into a sulphite complex such as $[Fe(SO_3)_2]'$, some of which would slowly undergo self-oxidation and -reduction with formation of dithionate but practically no sulphate (see Part 2). At low concentrations of ferrous salts the reaction chiefly follows course (i), which is largely independent of concentration, but higher concentrations help the higher-order reaction (ii) so that there is an increase in the proportion of dithionate.

It follows that if these deductions are sound we have a substantiated example, in the case of the ferrous reaction, of a catalysed oxidation which really is caused, in part at least, by a true alternating oxidation and reduction of the catalyst. It is also plain that such a mechanism is exceptional in the case of oxidations catalysed by metal salts and that, as a rule, the catalyst hands on the oxygen by a process which does not involve a true oxidation of the catalyst.

There are some unusual features about the results obtained with ferric sulphate and chloride (Table VI). In particular, the amount of oxidation occurring in the less concentrated chloride solutions is considerably greater than in comparable sulphate solutions. This is the opposite to what is found in other cases. The small increase in total oxidation in the most dilute sulphate solution appears to be a pure neutral salt effect since the proportion of dithionate formed is unaffected.

With higher concentrations of ferric sulphate, its reduction occurs with the high yield of dithionate characteristic of this reaction. A small catalytic effect due to the ferrous salt produced is probably superimposed on the primary reaction. There are no indications that the ferric ion has any direct catalytic action.

The greatly increased oxidation of sulphurous acid in the ferric chloride solutions suggests that the ferric salt is the oxidising agent in this case. It may well be that the $O_2\rightarrow$metal link is so weak in the case of ferric iron that an oxygen addition complex either is not formed at all with ferric salts or is very unstable. As soon as the ferric ion has been reduced by such reactions as have been discussed in Part 2 of this paper, then the ferrous ion formed would add oxygen with the consequences already discussed in connection with the oxidation catalysed by ferrous sulphate (Table V). This suggests that the oxidation shown in Table VI (*b*) is probably caused by alternate reduction and oxidation of ferric and ferrous complexes.

Cupric sulphate and chloride differ from all other salts we have examined in showing a marked poisoning action on the sulphurous acid oxidation at concentrations below about 0·025M. Above this concentration they show a positive catalytic action which can be quite marked even in 0·1M-solutions [Table VII (*a, b, c, d*)]. Both sulphate and dithionate formation are reduced by the poisoning action which is presumably caused by breaking of the normal oxidation chain.

This inhibiting action of very low copper concentrations is of particular interest because the cupric ion was selected by Franck and Haber (*loc. cit.*) as a possible agent for initiating the chain mechanism suggested by them. It may be that cupric ions could function in this way in much more dilute sulphurous acid solution than those examined by us, but it certainly appears as if any chain mechanism operating in these concentrated solutions must be started in some other way.

In concentrated sulphurous acid solutions the reactions with copper ions in presence of oxygen may be as follows : *

(A) $Cu^{\cdot\cdot} + 2SO_3'' \rightleftharpoons [Cu(SO_3)_2]''$

(B) $\left\{\begin{array}{l} 2[Cu(SO_3)_2]'' + H_2O = 2Cu^{\cdot} + SO_4'' + 3SO_3'' + 2H^{\cdot} \\ 2[Cu(SO_3)_2]'' = 2Cu^{\cdot} + S_2O_6'' + 2SO_3'' \end{array}\right.$

(C) $Cu^{\cdot} + 2SO_3'' \rightleftharpoons [Cu(SO_3)_2]'''$ $[Cu(SO_3)_2]''' + O_2 \rightleftharpoons [O_2\rightarrow Cu(SO_3)_2]'''$

(D) $[O_2\rightarrow Cu(SO_3)_2]''' + HSO_3 = Cu^{\cdot\cdot} + 2SO_4'' + HSO_3'$

(E) $[O_2\rightarrow Cu(SO_3)_2]''' = Cu^{\cdot} + 2SO_4''$

(F) $2[O_2\rightarrow Cu(SO_3)_2]''' + 2H^{\cdot} = 2Cu^{\cdot\cdot} + 3SO_4'' + SO_3'' + H_2O$

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* Although the concentration of SO_3'' would be low relatively to that of SO_3H', the SO_3'' seems more likely to be the constituent of the complex ions. Similar reactions could occur with complexes built up with SO_3H' ions but would be rather more complicated.

(A) Cupric ions are converted into complex sulphite anions.

(B) These complex anions undergo self-oxidation and -reduction, giving both sulphate and dithionate (Baubigny, *loc. cit.*).

(C) The cuprous ions formed in (B) are converted into oxygen–sulphite complex anions.

(D) This gives a possible way in which the normal oxidation chains are broken. In these chains the neutral HSO_3 is supposed to be the chief active agent.

(E) Most of the oxidation of sulphurous acid now proceeds by this mechanism.

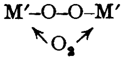
(F) Dithionate formation is never reduced to such a low value in the oxidation catalysed by copper salts as in that catalysed by manganese. This suggests that some cuprous copper is continually being reoxidised by reactions such as (F) and some dithionate being formed by reaction (B).

The above scheme seems to explain all the observed peculiarities of the oxidation catalysed by copper salts, and although it may appear to be complicated it is really made up of a number of quite simple reactions.

There is justification for the assumption of addition complexes containing molecular oxygen attached to metal atoms or ions. Several examples of complexes of this type can be cited : (1) the oxy-cobalt salts, *e.g.*, $[Co_2(NH_3)_{10}O_2](NO_3)_4$ and the anhydroxy-cobalt salts, *e.g.*, $[Co_2(NH_3)_{10}O_2](NO_3)_5$ (Fremy, *Annalen*, 1852, **83**, 227, 289; Werner, *Z. anorg. Chem.*, 1898, **16**, 245) furnish perhaps the most striking examples of complex salts containing co-ordinated molecular oxygen. Werner supposed that these compounds were true peroxides in which the oxygen was linked to each cobalt atom by a normal co-valency. This involved the assumption that in the anhydroxy-salts half of the cobalt had a valency of four and the other half of three; in the oxy-cobalt salts all the cobalt was tervalent. The reactions of these compounds are not in accordance with these assumptions, whereas they agree with the view that the oxy-cobalt compounds contain only bivalent cobalt while the anhydroxy-cobalt salts contain one atom of bi- and one of ter-valent cobalt. Thus Gluud, Keller, and Nordt (*Ber. Ges. Kohlentech.*, **1933**, **4**, 210) showed that, under suitable conditions, solutions of the oxy-cobalt salts break up on heating with almost quantitative regeneration of oxygen and *cobaltous* salt. Werner showed that after treatment of the anhydroxy-salts with concentrated hydrochloric acid 48% of the cobalt could be isolated as $[Co(NH_3)_5Cl]Cl_2$ while the rest could be obtained from the filtrate of the latter as cobaltous sulphate. Only 5% of the cobalt in the oxy-cobalt salts could be isolated as $[Co(NH_3)_5Cl]Cl_2$ but all the rest was obtainable as cobaltous sulphate. Hence the compounds are not true peroxides but must contain co-ordinated oxygen molecules as shown by the formulæ $[(NH_3)_5Co^{II}\leftarrow O_2\rightarrow Co^{II}(NH_3)_5](NO_3)_4$ and $[(NH_3)_5Co^{II}\leftarrow O_2\rightarrow Co^{III}(NH_3)_5](NO_3)_5$.

(2) In oxyhæmoglobin, molecular oxygen is presumably co-ordinated to the iron (ferrous) atom.

(3) According to Traube (*Ber.*, 1916, **49**, 1670) the tetroxides of the alkali and alkaline-earth metals are addition complexes of the peroxides and molecular oxygen, while the " ozonates " of the alkali metals are similar complexes of the alkali-metal hydroxides. The compounds could be formulated as



$$\underset{\nwarrow O_2 \nearrow}{M'-O-O-M'}$$

and $HO\cdot M^{I}\leftarrow O_2\rightarrow M^{I}-OH$

(4) Roberts (*Proc. Roy. Soc.*, 1935, *A*, **152**, 464) has shown that, by suitable treatment in oxygen a tungsten wire becomes coated with oxygen so that oxygen atoms cover about nine-tenths of the surface and oxygen molecules the remaining tenth. The oxygen molecules are driven off quite quickly when the wire is heated in a vacuum to about 80° but the atomic layer remains up to nearly 1700°.

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