210. *The Formation of Dithionate by the Oxidation of Sulphurous Acid and Sulphites.*

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The object of the present work was to obtain some insight into the nature of solutions of " sulphurous acid " and into the mechanism of dithionate formation.

Hydrolysis of Dithionic Acid.—Müller (*Bull. Soc. chim.*, 1909, **5**, 1119; 1911, **9**, 183), Yost and Pomeroy (*J. Amer. Chem. Soc.*, 1927, **49**, 703), Ishikawa and Hagisawa (*Sci. Rep. Tôhoku*, 1932, **21**, 484), and Goldfinger and von Schweinitz (*Z. physikal. Chem.*, 1933, [*B*] **22**, 117) have measured the rate of hydrolysis of dithionic acid in presence and in absence of oxidising agents. Since the latter do not affect the rate, it is concluded that the hydrolysis is irreversible. Our measurements in general confirm the results of these workers. The hydrolysis follows a unimolecular course, and the rate is directly proportional to the hydrogen-ion concentration. The constant $K = 2{\cdot}3/t[\mathrm{H}^{\cdot}] \cdot \log a/(a - x)$ (t being in seconds) has the value 4×10^{-8} at 15° and 5×10^{-4} at 100°. The hydrolysis had not previously been examined below 50°. In the experiment at 15°, 0·1*M*-dithionate and 5·9*N*-hydrochloric acid were used, and the hydrolysis was approximately unimolecular over a period of 128 days, during which 92·6% hydrolysis had occurred. It was evident from these experiments that, even if the hydrolysis were reversible, the position of equilibrium under any ordinary conditions would correspond to the presence of only a small proportion of dithionate.

Meyer (*Ber.*, 1902, **35**, 3439) failed to synthesise dithionic acid by the action of sodium sulphite or bisulphite on ferrous or manganous sulphates in presence of dilute sulphuric acid. We attempted its synthesis from the products of its hydrolytic decomposition under the most varied conditions of temperature, concentration, acidity, and relative proportions of sulphurous and sulphuric acids or of sulphite and sulphate and acid. Many of the mixtures were analysed at intervals over long periods of time. All the experiments gave negative results and need not be quoted in detail. Attention is, however, directed to Expt.

G which has a bearing on the matter. We conclude, therefore, that the hydrolytic decomposition of dithionic acid is definitely irreversible. Moreover, we repeated the experiment of Baumgarten (*Ber.*, 1932, **65**, [*B*], 1645), who stated that dithionate is formed in relatively large amounts by the action of potassium pyrosulphate on a solution of potassium pyrosulphite and bicarbonate, but failed to detect any dithionate. Our pyrosulphite was carefully selected, large, clear crystals, almost entirely free from opaque oxidised material: this is important, since such material contains about 24% of potassium dithionate (see p. 916); however, Baumgarten's yields of supposed dithionate seem to be too great to have originated in this way.

Oxidation of Sulphurous Acid by Chlorine, Iodine, or Hydrogen Peroxide.—It is important to note that all oxidising agents are without action upon dithionic acid unless conditions are such as to cause its hydrolysis. The non-appearance of dithionic acid among the oxidation products of sulphurous acid by any given oxidant cannot therefore be explained, as has sometimes been attempted, by supposing that it was first formed and then further oxidised to sulphate.

Chlorine, iodine, and hydrogen peroxide all appear to yield traces of dithionate in the oxidation of sulphurous acid (Expts. A and C), but the amount is very small even when concentrated solutions are used. Oxidation of pyrosulphite solutions gives the highest yield of dithionate, just as in the case of atmospheric oxidation. For these experiments, we used both the potassium and the sodium salt, but the former is more suitable as it is obtained more readily in large crystals, which can be freed almost entirely from any oxidation product, but even perfectly clear unoxidised crystals may contain appreciable amounts of dithionate, for which allowance must be made (Expt. B). The sodium salt appears to contain much more dithionate, and even sodium sulphite heptahydrate crystals are liable to contain traces (Expt. B).

The results of Expt. C seem to show that iodine produces a small amount of dithionate. The proportion of dithionate to sulphate appears to be very sensitive to the experimental conditions and to vary with acidity and concentration in the same sort of way as when gaseous oxygen is the oxidising agent. The largest amount of dithionate formed in the iodine experiments corresponded to only about 0·8% of the total oxidation.

The usual method of estimating sulphurous acid or sulphites by addition to excess of standard iodine and back titration with thiosulphate must give slightly low results for total sulphur dioxide. The error would be equal to half the percentage of dithionate formed by the iodine, and under ordinary conditions of analysis would probably approximate to 0·1% so far as can be judged from the results of Expt. C.

Hydrogen peroxide acting upon potassium pyrosulphite also produced small amounts of dithionate, but the largest amount obtained only corresponded to about 1% of the sulphite oxidised (Expt. C); the crystallised normal sodium sulphite afforded no trace of dithionate.

Volhard (*Annalen*, 1887, **103**, 242), Spring and Bourgeois (*Bull. Soc. chim.*, 1886, **46**, 151; 1891, **6**, 920; *Arch. Pharm.*, 1891, **229**, 707), and Otto (*ibid.*, p. 171; 1892, **230**, 1) found that oxidation by iodine produced only sulphate. Thénard (*Ann. Chim. Phys.*, 1818, **8**, 306) and Meyer (*Ber.*, 1901, **34**, 3606) found that hydrogen peroxide yielded only sulphate, but Nabl (*Monatsh.*, 1901, **22**, 737) stated that when acting upon a large excess of barium sulphite, it always formed a little dithionate.

The Oxidation of Sulphurous Acid and Sulphites by Free Oxygen.—Little attention has been paid to the formation of dithionate during the oxidation of sulphurous acid and its salts by free oxygen, and although Franck and Haber (*Ber. Berl. Akad.*, 1931, 250) and Haber and Wansbrough-Jones (*Z. physikal. Chem.*, 1932, [*B*], **18**, 103) attached great importance to its formation in connection with their theory of the chain mechanism of sulphite oxidations, yet they did not conclusively demonstrate the point. We have now separated and identified the dithionate as the potassium salt (Expt. D).

Mineral acid greatly retards the rate at which sulphurous acid reacts with free oxygen, which makes it likely that free sulphur dioxide in the aqueous solution is not directly oxidised in this case.

Expt. E and Tables II and III give our results obtained in the oxidation of sulphurous acid and sodium pyrosulphite with free oxygen. They show that the proportion of dithionate produced depends to a large extent upon the concentration of total sulphur dioxide, and, in a general way, increases with this. Up to a point, increase in acidity is favourable to dithionate formation, so that for each sulphur dioxide concentration there is an acidity which leads to a maximum proportion of dithionate. With progress of the reaction, acidity increases and total sulphur dioxide decreases, so the maximum proportion of dithionate is generally formed, not at the beginning of the oxidation, but at a later stage or, in dilute solutions, near the end.

The proportion of sulphate and dithionate formed remains essentially the same when the atmospheric oxidation is carried out in a waxed bottle [Expt. E (ii)]. This shows that in all probability neither sulphate nor dithionate formation is due to a reaction occurring at the glass–solution interface.

We have shown that oxidation of solutions of sodium sulphite by oxygen follows a unimolecular course and that no dithionate is produced.

It is stated by Foerster, Brosche, and Norberg-Schulz (*Z. physikal. Chem.*, 1924, **110**, 476) that potassium pyrosulphite is stable, and although this may be true for dry crystals exposed to dry air, it is incorrect if they are subject to moist air, for then they oxidise at an appreciable rate. We have found that the oxidation product is not sulphate, as is usually stated, but a mixture of sulphate and dithionate containing about 24% of the latter: on the other hand, a saturated solution of sodium pyrosulphite gives a maximum yield of about 9% of dithionate (see Table III). A possible explanation of this difference is given on p. 918.

Oxidation of Pyrosulphites.—The oxidation of solutions of sodium pyrosulphite is described in Expt. E (iii), and the results are given in Table III. The ratio of dithionic acid to total oxidised sulphur dioxide increases rapidly at first with increasing concentration, then slows down and becomes nearly constant in concentrated solution.

Old bisulphite solutions which have been exposed to air may contain large amounts of dithionate in addition to sulphate. A 6—10-year old sample of " ammonium bisulphite " in a stoppered bottle had deposited much solid ammonium sulphate and sulphur as a result of the photochemical change $3H_2SO_3 \longrightarrow 2H_2SO_4 + S + H_2O$, and much dithionate and sulphate had been formed also by atmospheric oxidation. A complete analysis of the mixture was made (Expt. F). Allowing for sulphate formed in conjunction with sulphur by the above reaction, it was found that 25·6% of the sulphur dioxide which had suffered atmospheric oxidation had yielded dithionate. The total sulphur and sulphur compounds present in the mixture showed that the solution was initially about 18*N*, so the high yield of dithionate is reasonable when compared with the results obtained with sodium pyrosulphite. The above assumption, that all the dithionate had resulted from atmospheric oxidation and none from the photochemical change, was justified by the results of Expt. G, in which an approx. 16*N*-ammonium bisulphite solution in a sealed tube was exposed to diffuse daylight for 4 years: 90·6% of the sulphurous acid had then decomposed to sulphur and sulphuric acid, but no dithionate could be detected. A similar solution kept in the dark slowly underwent the same change, but a trace of dithionate appeared to be formed. The absence of dithionate is important, not only from the point of view of the above photochemical change, but also because it supports the view that synthesis of dithionate from sulphate and sulphite is not possible, for if so, some should have been formed in both tubes of Expt. G.

Oxidation of Solid Pyrosulphite and Sulphite.—Examination of a 20-year old specimen of large crystals of potassium pyrosulphite kept in a corked bottle showed that it was largely converted into opaque pseudomorphs. The oxidised product forming most of the crystals was approximately homogeneous throughout, as shown by analysis of different layers, and consisted of a mixture of sulphate and dithionate, the latter representing 23—24% of the sulphur dioxide oxidised. There was also a very small proportion of potassium hydrogen sulphate. Finely powdered pyrosulphite yields much less dithionate (2·35%), because much of the dioxide escapes before oxidation occurs.

In a very dry atmosphere (over calcium chloride or sulphuric acid) no oxidation occurs even in pure oxygen. The drier the atmosphere the slower the oxidation but the higher the proportion of dithionate, probably because escape of sulphur dioxide is correspondingly slower; for instance, after 3 years' exposure of large crystals of potassium pyrosulphite in Khartoum, where the relative humidity of the air is very low, especially for 9 months in the year, the oxidised layer contained dithionate corresponding to 29% of the total oxidised sulphur dioxide. This is not a temperature effect, for lower values for dithionate are found, even in Khartoum, in an artificially moistened atmosphere.

A 20-year old sample of sodium sulphite heptahydrate powder was found to consist of Na_2SO_3, 12·43; Na_2SO_4, 54·85; $Na_2S_2O_6$, 0·07%, the balance being water. On the assumption that there was originally 0·028% of $Na_2S_2O_6,2H_2O$ (see Expt. B), it appears that only 0·065% of the oxidised sulphite is dithionate.

Oxidation by Permanganate and Dichromate.—Both dithionate and sulphate are formed when sulphurous acid is oxidised by permanganate in acid solution (Péan de St. Gilles, *Ann. Chim. Phys.*, 1859, **55**, 374). Berthier (*ibid.*, 1843, **7**, 77) first showed that some dithionate is formed during the oxidation of sulphurous acid by chromic acid. The reaction was further examined by Bassett (J., 1903, **83**, 692), who found that about 9—11% of the sulphurous acid oxidised yielded dithionate, the proportion being apparently independent of concentration, temperature, and acidity, as in the case of the permanganate reaction (Dymond and Hughes, J., 1897, **71**, 314). More recent experiments indicate that the above figure was too high and should be reduced to about 4%.

The constancy in the proportion of dithionate formed under varying conditions by the two oxidising agents is very remarkable and it seemed desirable to examine the matter more fully. The dithionate formed in the chromic acid reaction was isolated as the potassium salt (Expt. H).

Various methods were tried for determining the exact proportion of dithionate formed in these reactions, and the influence of concentration and acidity. Atmospheric oxidation is hard to eliminate completely because any dissolved oxygen is activated by the other reactions (Expt. I). If sulphurous acid is added in excess to potassium dichromate without the previous addition of sufficient sulphuric acid, some of the sulphite becomes masked so that it is subsequently only slowly oxidised by iodine (see Bassett, *loc. cit.*). To avoid error on this account several hours should elapse before titration of excess iodine. Several series of volumetric experiments were made (Expt. J), and in one series liquid sulphur dioxide was used in order to eliminate uncertainties due to its solution. The results thus obtained are probably the most accurate afforded by volumetric methods.

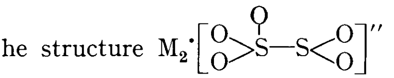
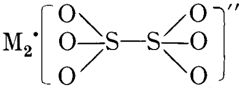
In other series of experiments the dithionate formed was determined gravimetrically (Expt. K). These estimations are probably more accurate than the volumetric, although they have the disadvantage that a very large amount of precipitate has to be separated before one can determine the dithionate.

It seems clear that, within the limits of accuracy of the experiments, the proportions of dithionate and sulphate formed in the dichromate and the permanganate reaction are unaffected by variations in the concentration or acidity of the reactants. A consideration of all the results indicates that for the dichromate reaction approximately 4% of the sulphur dioxide oxidised is converted into dithionate, while for the permanganate reaction the proportion is 18 or 19%.

When excess of strongly acid permanganate was used, a normal value for dithionate formation was obtained (18·85%), but when excess of neutral permanganate reacted with solid potassium pyrosulphite a much higher proportion (24·1%) was formed. Under these conditions insufficient acid was present to permit complete reduction to manganous salt ($2KMnO_4 + 2K_2S_2O_5 = 3K_2SO_4 + MnSO_4 + MnO_2$). This at first sight appears to indicate that a higher proportion of dithionate is formed in the reduction stage $MnO_4' \longrightarrow MnO_2$ than in the stage $MnO_2 \longrightarrow Mn^{\cdot\cdot}$, but this can hardly be, since the latter stage is said to yield about 70% dithionate (Carpenter, J., 1902, **81**, 1; Spring and Bourgeois, *loc. cit.*). It seems, then, safer to say that the former stage yields more dithionate than does the complete reduction $MnO_4' \longrightarrow Mn^{\cdot\cdot}$. This suggests that the complete reduction of permanganate by sulphurous acid does not normally involve the stage $MnO_2 \longrightarrow Mn^{\cdot\cdot}$. The formation of the dioxide under acid conditions is probably due to oxidation of manganous by permanganate ions.

Discussion.

Any explanation of the mechanism of the oxidation of " sulphurous acid " must take into account the following facts. (1) Oxidation of alkaline solutions of sulphites usually produces only sulphate. (2) Solid alkali pyrosulphite on atmospheric oxidation yields a high percentage of dithionate, whereas solid normal alkali sulphite yields the merest trace. (3) Sulphurous acid and acid sulphite solutions yield on atmospheric oxidation mixtures of sulphate and dithionate, the proportion of the latter increasing rapidly with the concentration of the solution and also depending on the acidity : for each concentration of sulphurous acid there is an acidity at which there is a maximum yield of dithionate. (4) Oxidation of sulphurous acid by chlorine, iodine, or hydrogen peroxide produces mainly sulphate and very little dithionate, the proportion of which appears to depend upon concentration and acidity. (5) Potassium permanganate and dichromate in acid solution oxidise sulphurous acid in rapid homogeneous reactions to produce a mixture of sulphuric and dithionic acids in proportions which are different in the two cases but remain constant in each case over a wide range of concentrations and acidities. In alkaline solution, permanganate gives only sulphate (Fordos and Gélis, *J. Pharm.*, 1859, **36**, **113**; Péan de St. Gilles, *loc. cit.*; Hönig and Zatzek, *Monatsh.*, 1883, **4**, 738).

All these facts seem to admit of a satisfactory and consistent explanation on the following lines : From (1) we conclude that the sulphite ion never yields anything but the sulphate ion on oxidation. There is *X*-ray evidence to show that the alkali pyrosulphites have the structure  $M_2^{\cdot}\left[\begin{matrix}O\\O\end{matrix}\!>\overset{O}{S}-S<\begin{matrix}O\\O\end{matrix}\right]''$ (Zachariasen, *Physical Rev.*, 1932, **40**, 923), and it must be concluded that they are oxidised directly to dithionate with the structure  which again agrees with the *X*-ray evidence (Huggins and Frank, *ibid.*, 1928, **31**, 916; *J. Min. Soc. Amer.*, 1931, **16**, 580; Helwig, *Z. Krist.*, 1932, **83**, 485; Hägg, *ibid.*, p. 265).

Oxidation of sulphurous acid solutions by free oxygen is a chain reaction occurring in the bulk of the solution. This may be assumed to contain proportions of SO_2, SO_3'', S_2O_5'', H_2SO_3, $H_2S_2O_5$, HS_2O_5', HSO_3' (sulphonic), and $HO{\cdot}SO_2'$ (sulphurous) which depend upon the total sulphur dioxide concentration and upon the p_H. The only constituents identifiable by spectroscopic methods are SO_2, HSO_3', and SO_3'' (Albu and Goldfinger, *Z. physikal. Chem.*, 1932, [*B*], **16**, 338), but according to Fadda (*Nuovo Cim.*, 1932, **9**, 227) only S_2O_5'' and not HSO_3' frequencies occur in the Raman spectra of sodium bisulphite solutions. If the reasonable assumption is made that $H_2S_2O_5$ is a stronger acid than H_2SO_3, and that HS_2O_5' is stronger than HSO_3', then increase in acidity will favour pyrosulphite species (*i.e.*, S_2O_5'', HS_2O_5', and $H_2S_2O_5$) at the expense of sulphite species (*i.e.*, SO_3'', HSO_3', and H_2SO_3). As oxidation by free oxygen proceeds, the solution becomes more acid as sulphuric and dithionic acids replace the weaker sulphurous and pyrosulphurous acids, and the proportion of dithionate formed should increase if it results from direct oxidation of pyrosulphite species. On the other hand, total sulphur dioxide diminishes as oxidation proceeds, and this favours a shift of the sulphite equilibria in the opposite direction. These two opposing effects will lead to a maximum in the dithionate/sulphate ratio at some intermediate stage in the oxidation.

The observations made on the atmospheric oxidation of solid alkali pyrosulphites agree with the view that oxidation occurs in an adsorbed moisture film. Since this is bounded on one side by solid pyrosulphite with which the reaction chains would be involved, the production is explicable of a higher proportion of dithionate than in a very concentrated homogeneous solution, in which much of the pyrosulphite is hydrolysed.

Franck and Haber (*loc. cit.*), Haber and Wansbrough-Jones (*loc. cit.*), and Albu and von Schweinitz (*Ber.*, 1932, **65**, 729) interpret the photochemical decomposition of sulphurous acid or sulphites and their oxidation by free oxygen and most other reagents in terms of reaction chains involving neutral HSO_3 or singly charged SO_3'. Dithionate formed in such reactions is supposed to result from dimerisation of HSO_3 or SO_3', which causes breaks in the chain. These assumptions do not seem adequate to explain our results. In any case we could not find evidence of dithionate formation either in the oxidation of dissolved sodium sulphite by free oxygen, or in the photochemical decomposition of bisulphite solutions in absence of free oxygen (Expt. G).

The traces of dithionate formed in the atmospheric oxidation of solid crystallised sulphite are due, we think, to oxidation of small amounts of S_2O_5'' present in the solution or moisture film in which the oxidation occurs; the aqueous solution of the sulphite is alkaline to litmus owing to hydrolysis, and the presence of pyrosulphite in the saturated solution film appears highly probable. The p_H of concentrated solutions is between 9·5 and 10. We would ascribe a similar origin to the small amounts of dithionate found by Nabl (*loc. cit.*) in the action of hydrogen peroxide on barium sulphite.

The photochemical decomposition studied by us evidently differed from that considered by Haber, since free sulphur and not free hydrogen was liberated. According to Haber and Wansbrough-Jones (*loc. cit.*), the formation of dithionate by anodic oxidation is also due to the same reaction chains mentioned above and to dimerisation of neutral HSO_3. It seems that Franck and Haber's chain mechanism could be improved by including a step such as $HSO_3 + O_2 + S_2O_5'' + H_2O = SO_4'' + S_2O_6'' + OH + 2H^{\bullet}$, in which the S_2O_5'' ion is oxidised.

Formation of dithionate by permanganate and dichromate cannot be due to oxidation of $H_2S_2O_5$ or S_2O_5'' for in that case it would depend upon the concentration and acidity, neither can the sulphate and dithionate result from independent oxidation of sulphurous acid, H_2SO_3,and of sulphonic acid, $HO{\cdot}SO_2H$, to sulphuric and dithionic acids respectively, for although the proportion of these would be independent of the concentration * the rate at which the latter would be formed would be expected to fall off with dilution far more quickly than would the rate of formation of the former, which would, presumably, be a reaction of a lower order. The experimental results can be accounted for by supposing that a complex addition product is first formed very rapidly from the permanganate or dichromate and sulphurous acid, or from some intermediate stage in the reduction of the oxidant, and then decomposes, also very rapidly, by self-oxidation and -reduction in two different and independent manners to yield both sulphate and dithionate. Experimental evidence of such a two-stage reaction is to be found in the action of sulphurous acid on freshly precipitated ferric hydroxide, the first product being a reddish solution of complex ferric sulphite which slowly bleaches with a nearly quantitative yield of dithionate and only a very small amount of sulphate (Berthier, *loc. cit.*; Gélis, *Bull. Soc. chim.*, 1863, **5**, 333; *Ann. Chim. Phys.*, 1862, **65**, 222; Seubert and Elten, *Z. anorg. Chem.*, 1893, **4**, 86; Meyer, *Ber.*, 1901, **34**, 3606; Carpenter, *loc. cit.*).

That a complex sulphite ion is involved in these reactions is also shown by the behaviour of silver sulphite; when prepared by addition of sodium sulphite solution to excess of silver nitrate, it forms a white precipitate which is only slowly affected by boiling with water. It is soluble in ammonia giving a solution which appears to be stable towards heat. The silver sulphite dissolves in sodium sulphite solution, and on warming, the metal is all rapidly precipitated, a large amount of dithionate being formed (Baubigny, *Compt. rend.*, 1909, **149**, 735, 858; 1910, **150**, 466).

With metals like silver, copper, or ferric iron, there can readily arise anionic complex sulphite ions such as $[Ag(SO_3)_2]'''$ or $[Fe(SO_3)_3]'''$. Complexes of this type are evidently likely to undergo self-oxidation and -reduction if the metal ion is easily reducible to metal or to a lower valency stage.

If two SO_3'' ions of such complexes each surrender an electron to the metal ions, the SO_3' groups could readily link up to form the dithionate ion. In the cases mentioned at least two complexes would be involved. It is just as easy, however, for sulphate to be formed by a similar mechanism. The SO_3'' ion loses an electron to the metal ion, and on collision with another complex the second electron is lost by the partially discharged sulphite group and neutral SO_3 results, which at once reacts with water to give sulphuric acid.

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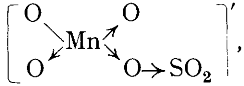
* Since they are related by the equation $(HO)_2SO \rightleftarrows HO{\cdot}SO_2H$.

Since the same complex gives rise to either sulphate or dithionate by reactions of the same order, it follows that the proportion of the two oxidation products should be essentially independent of concentration, acidity, etc., and depend almost entirely upon the nature of the oxidising metal ion. As, moreover, this mechanism yields dithionate by oxidation of bound *sulphite ions*, there is no reason why it should not operate sometimes under alkaline conditions. This happens with cupric salts (Baubigny, *Ann. Chim. Phys.*, 1910, **20**, 12; *Compt. rend.*, 1912, **154**, 701; Albu and von Schweinitz, *loc. cit.*).

Permanganic and chromic (or dichromic) acids could give rise to complex sulphite anions of the heteropolyacid type by addition of one or more sulphur dioxide molecules to the MnO_4', CrO_4'', or Cr_2O_7'' ion. Such complexes, *e.g.*,  $\left[\begin{array}{ccc}\mathrm{O} & & \mathrm{O}\\ & \searrow\mathrm{Mn}\nearrow & \\ \mathrm{O} & \swarrow\quad\searrow & \mathrm{O}\rightarrow\mathrm{SO_2}\end{array}\right]'$, would clearly be very unstable and could break down, in precisely the same way as those previously considered, to yield either sulphate or dithionate, both of which can be regarded as formed by oxidation of *sulphur dioxide*, not of sulphite ions or pyrosulphite.

Decomposition of a sulphite complex could only give rise to dithionate in cases where just one electron is absorbed from an SO_3'' by the metal ion. If two were absorbed, the sulphur trioxide so formed could only yield sulphate, for we have been unable to produce dithionate from sulphite and sulphate. This renders it likely that any reduction of a metal ion by two valency units, *e.g.*, $Pb^{\cdot\cdot\cdot\cdot} \longrightarrow Pb^{\cdot\cdot}$, would yield only sulphate. It appears that lead peroxide absorbs sulphur dioxide fairly readily with formation of the sulphate only (Wilsdon and McConnell, *J. Soc. Chem. Ind.*, 1934, **53**, 385T).

According to Rammelsberg (*Pogg. Ann.*, 1846, **67**, 504), mercuric oxide yields no dithionate, and this may be for the above reason, since the mercurous ion formed as an intermediate step in the reduction by sulphite is considered to be a complex " mercuric " ion $[Hg\rightarrow Hg^{\cdot\cdot}]$. Its formation therefore corresponds to reduction of half of the mercuric ions to neutral mercury atoms in one step, followed by co-ordination of the neutral atoms to mercuric ions.

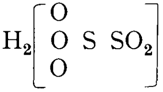
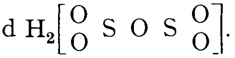
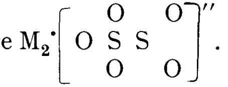
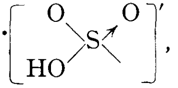
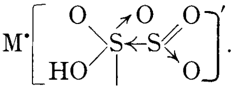
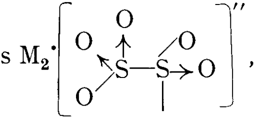
Manganese dioxide affords a large yield of dithionate, and since the tervalent stage of manganese is well defined, it is probable that the reduction occurs in the two steps. On the other hand, it is also possible that in some circumstances the one-stage reduction $Mn^{\cdot\cdot\cdot\cdot} \longrightarrow Mn^{\cdot\cdot}$ may also occur, yielding only sulphate. This may account for the puzzling statements in the literature as to the effect of various pre-treatments of the dioxide upon the yields of dithionate. If the reaction always went in the two stages by the complex sulphite-ion mechanism, we should have expected the proportion of dithionate formed to be nearly independent of conditions such as concentration of sulphurous acid, acidity, temperature, state of division, etc., whereas it is stated to be largely dependent upon some of them (Heeren, *Pogg. Ann.*, 1826, **7**, 55; Spring and Bourgeois, *Bull. Soc. chim.*, 1886, **46**, 151; Spring's " Collected Researches," p. 1123).

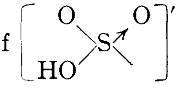
The possibility that two SO_3'' ions in one complex ion such as $[Mn(SO_3)_3]''$ could each lose one electron to the $Mn^{\cdot\cdot\cdot\cdot}$ ion at the same instant of time and then unite to give S_2O_6'' seems much less likely than that the two halves of the S_2O_6'' come from two separate complexes.

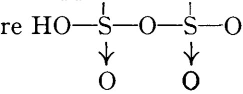
Dithionate can also be formed in alkaline solution by electrolytic oxidation, and we believe that this process is essentially similar to that occurring in the complex-sulphite-ion mechanism just discussed. The only difference is that the SO_3'' ion surrenders either one or two electrons to the solid metal of the positive electrode instead of to a metal ion. If two SO_3'' ions each lose one electron and collide immediately before or after that event, a dithionate ion results. If, however, SO_3'' loses both electrons, sulphate is formed. The oxidation on this interpretation is purely electrochemical. Glasstone (J., 1933, 829) considers that the dithionate is a secondary product due to oxidation of sulphite by hydrogen peroxide formed electrochemically, but direct experiment did not support this view, for he could only obtain 1—2% of dithionate by the action of hydrogen peroxide on sulphite. Even this yield was probably fallacious and due to dithionate present in the potassium pyrosulphite used as the source of sulphite ions. We could find no production of dithionate in the action of hydrogen peroxide on sodium sulphite (Expt. C), and only 0·5—1% was formed when 3*N*-hydrogen peroxide acted upon solid potassium pyrosulphite, the conditions most likely to give the best yield of dithionate.

Glasstone's decision against the purely electrochemical origin of dithionate in the electrolytic oxidation was based upon the effect of various anodic treatments upon the yield of dithionate, and upon the fact that the addition of catalysts which decompose hydrogen peroxide reduced the yield of dithionate. It seems to us that these factors may equally well affect the proportions in which the sulphite ion undergoes single or double discharge, and hence would affect the dithionate : sulphate ratio in the oxidation products (see p. 919). The singly charged SO_3' would doubtless remain attached to the electrode until it reacted with water or until an SO_3'' ion came sufficiently close to link up with it, after itself losing an electron. For this reason the rate of formation of dithionate would only depend upon the first power of the sulphite concentration, as does the rate of formation of sulphate. This explains why the ratio of dithionate to sulphate was practically independent of the sulphite concentration in Glasstone's experiments, a fact which was not explained by his theory.

The singly charged SO_3' would also tend to react with water: $SO_3' + HOH \longrightarrow HSO_3' + OH$. Any factor which facilitates the liberation of oxygen from hydroxyl ($2OH = H_2O + O$; $2O = O_2$) would tend to favour this mode of reaction of the SO_3' and so diminish the amount of dithionate formation. It seems likely that catalysts which decompose hydrogen peroxide would also catalyse this decomposition of hydroxyl, and this may be another reason for the effect of such catalysts observed by Glasstone.

Structure of Pyrosulphurous Acid.—The yellow solutions obtained by saturating concentrated alkali-metal or ammonium bisulphite solutions with sulphur dioxide have been previously explained on the basis of a compound  $H_2\left[\begin{matrix}O\\O\ S\ SO_2\\O\end{matrix}\right]$ isomeric with pyrosulphurous acid  $H_2\left[\begin{matrix}O\\O\end{matrix}\ S\ O\ S\ \begin{matrix}O\\O\end{matrix}\right]$. The yellow isomeride was considered to owe its colour to the presence of a 10-electron sheath on the sulphur atom to which the sulphur dioxide becomes attached (Bassett and Durrant, J., 1927, 1409). This explanation is at first sight opposed to the view now held that the solid pyrosulphites (metabisulphites)—which are colourless—have the structure  $M_2^{\cdot}\left[\begin{matrix} & O & O\\ O & S & S\\ & O & O\end{matrix}\right]''$. We do not consider that this is the case, however. No solid yellow pyrosulphites are known, the yellow compounds only being formed in aqueous solutions which are strongly acid, so that it is reasonable to suppose that they are themselves acids or potential acids. On the assumption that alkali hydrogen sulphite may be written , the yellow addition compound is regarded as . It seems very probable that this structure with the decet of electrons on the one sulphur atom would become unstable if the hydrogen atom ionises or is replaced by ionic M˙. The flux of electrons is then reversed, with formation of the colourless , in which both sulphur atoms have octets.

Owing to the instability of sulphurous acid, a sufficient concentration of  ion for visible formation of the yellow complex ion can only be obtained in presence of considerable concentrations of alkali or ammonium sulphite. Were sulphurous acid sufficiently stable, one would have expected the formation of the yellow compound to occur more readily from the un-ionised acid than from the HSO_3' ion, but actually, yellow sulphurous acid solutions cannot be obtained in absence of sulphites.

If the above view of the nature of the yellow acid and of its isomerism with the colourless pyrosulphite is accepted, it does not appear so necessary to suppose that a colourless pyrosulphurous acid with the structure  $\mathrm{HO{-}\underset{\underset{O}{\downarrow}}{\overset{|}{S}}{-}O{-}\underset{\underset{O}{\downarrow}}{\overset{|}{S}}{-}OH}$ also exists.

It is well known that the oxidation of sulphurous acid and sulphites by gaseous oxygen is very sensitive to the influence of catalysts, both positive and negative (cf. Meyer, *Ber.*, 1887, **20**, 3058; Titoff, *Z. physikal. Chem.*, 1903, **45**, 641; Reinders and Vlès, *Rec. trav. chim.*, 1925, **44**, 249; Bigelow, *Z. physikal. Chem.*, 1898, **26**, 493; Moureu and Dufraisse, *J. Soc. Chem. Ind.*, 1928, **47**, 819, 848). The oxidation is accelerated by light, the efficiency being of the order of 50,000 molecules per quantum. High quantum yield and susceptibility to the action of inhibitors are two important characteristics of chain reactions, and there seems no doubt that the oxidation of sulphite and sulphurous acid by gaseous oxygen follows a chain mechanism (Bäckström, *J. Amer. Chem. Soc.*, 1927, **49**, 1460; *Trans. Faraday Soc.*, 1928, **24**, 714; Christiansen, *ibid.*, p. 714; Alyea, *J. Amer. Chem. Soc.*, 1930, **52**, 2743).

The chain mechanism gives the best explanation of the results obtained in the following experiments. Methylene-blue is reduced, comparatively slowly, by sulphurous acid, the leuco-base and sulphuric acid being formed. Since the leuco-base is fairly rapidly reoxidised by free oxygen, it was thought that the oxidation of sulphurous acid by oxygen might be positively catalysed by methylene-blue. Strong inhibition was, however, found [Expt. L, Table VI (*a*) and (*b*)], whilst it also appeared that the bottle in which methylene-blue had been used had been " poisoned." This suggested that the oxidation of sulphurous acid was a surface reaction occurring on the glass–solution interface, but as it was found that oxidation occurred at the same rate in a bottle which had been well coated internally with paraffin wax as in an uncoated bottle (Expt. M), this view had to be abandoned. Methylene-blue inhibited the reaction just as effectively in the waxed as in the unwaxed bottle and the former also became poisoned. This poisoning effect seemed to support the view that the reaction was a surface one, but it was found that the methylene-blue or the leuco-base is not at all readily removed completely from the bottles. This, no doubt, is due to adsorption on the glass surface, with the result that a small quantity passes into any fresh solution which is introduced and inhibits its oxidation. The oxidation of sulphurous acid seems to be very sensitive to traces of methylene-blue or the leuco-base which acts either as a direct interruptor of the chain mechanism or as a poison to some positive catalyst such as copper ions present in minute amount in the solution.

Experiment showed that the methylene-blue removed by washing from a " poisoned " bottle would inhibit oxidation of sulphurous acid in another bottle. The leuco-methylene-blue formed by the action of sulphurous acid was much more strongly adsorbed by the glass than methylene-blue itself. Since oxidation is inhibited in the completely decolorised solutions it is fairly certain that it is leuco-dye rather than the dye itself which is the actual inhibitor.

Repeated (six) washings with water, allowing opportunity for oxidation of the leuco-base, followed by several with alcohol and then one with water, removed the methylene-blue sufficiently for oxidation of sulphurous acid to proceed again at a normal rate in a previously " poisoned " bottle even in the initial stages. The precise mechanism of the " poisoning " of the *waxed* bottles is not clear. Normal adsorption on the non-polar wax surface seems unlikely, as does true solution of methylene-blue or its leuco-compound in the wax. Possibly sufficient becomes occluded in hollows and bubbles or sufficient may be flocculated from the solution on to the wax to be able to withstand several rinsings with cold water and so give rise to the observed poisoning effect. A " poisoned " bottle gradually recovers (Expt. M)

When a very dilute solution of methylene-blue is treated with sulphur dioxide it is slowly bleached. If, after several days' exposure to the air, the gas is removed by a current of air, methylene-blue is regenerated, but the amount so regenerated decreases with each repetition of the experiment, and the titanous chloride required to discharge the blue colour decreases. It would appear therefore that the inhibitor, leuco-methylene-blue, or methylene-blue itself is slowly oxidised in a coupled reaction with the sulphurous acid to some colourless or less blue product which neither reacts with titanous chloride nor inhibits the oxidation of sulphurous acid. This explains the slow recovery of "poisoned" bottles. The time needed for such recovery would depend upon the amount of inhibitor present initially. Slow oxidation of substances which act as inhibitors to oxidation is a general phenomenon (cf. Bäckström, *Trans. Faraday Soc.*, 1928, **24**, 601).

Although the inactive oxidation product is blue, it loses its colour when treated with excess of sulphur dioxide. This is probably a bleaching effect of acid due to salt formation similar to that of strong acids on many basic dyes.

EXPERIMENTAL.

Estimation of Dithionic Acid.—Examination of the methods available showed that complete oxidation to sulphate by nitric acid was readily obtainable in spite of Baubigny's statements (*Compt. rend.*, 1909, **149**, 1069). We applied the method as follows. Sulphur dioxide was first removed by a current of air-free carbon dioxide, and sulphate by very slow addition of barium chloride solution in small excess at about 60° with constant mechanical stirring; after standing over-night, the precipitate was filtered off and washed, and filtrate and washings were well mixed and kept over-night, any small deposit of barium sulphate being then removed, and the solution evaporated to dryness with 15 c.c. of concentrated nitric acid per 200 c.c. It was essential to carry out careful blank determinations in all cases. The second over-night standing is especially necessary when analysing solutions containing potassium, for considerable adsorption of its sulphate by barium sulphate may occur, and, although it may be partly removed during the washing, yet frequently this occurs after most of the excess barium chloride has been removed.

Higher polythionates if present must be removed either by silver nitrate, followed by barium chloride, or by chlorine or bromine water, followed by barium chloride. The bromine-water method is the best and most convenient.

Experiment A. (*Theory, p.* 915.)—1 L. of 1·062*N*-sulphurous acid was oxidised at 30—40° by chlorine from a cylinder, and the small excess of gas removed by a rapid air current. The greater part of the sulphate and chloride were removed by treatment with solid lead carbonate, and lead was removed from the filtrate by sodium carbonate; only 0·004% of the sulphur dioxide oxidised had yielded dithionate. In precisely similar experiments with 1·4*N*- and *N*-sulphurous acid and solid iodine, the corresponding values were 0·011 and 0·017%.

Experiment B. (*Theory, p.* 915.)—Large crystals of potassium pyrosulphite, after careful removal of oxidised material, were dissolved in air-free *N*-hydrochloric acid, and the sulphur dioxide displaced by a current of carbon dioxide. Sulphate and dithionate were estimated in the solution in the ordinary way. After deducting from the dithionate so found the amount which would have accompanied the sulphate in oxidised material, it was concluded that the clear, unoxidised crystals contained 0·38% of dithionate. Several entirely different samples gave almost identical results.

In the same way, a sample of the sodium salt was shown to contain 0·91% of the dithionate, and even clear crystals of sodium sulphite contained 0·028%, which is not due to experimental uncertainty.

Experiment C. (*Theory, pp.* 915, 920.)—The potassium pyrosulphite used in the experiments with iodine or hydrogen peroxide (Table I) was well scraped to remove oxidised material before being weighed. In each of the iodine experiments, about 2·5 g. of iodine and 4 g. of potassium iodide in about 5 c.c. of solution were used, and analyses were carried out as follows: Iodide was precipitated by addition of silver nitrate, and the excess of silver and the sulphate by addition of barium chloride, both precipitations being made in the cold. After standing over-night, the clear liquid was filtered, and the precipitate washed with several small quantities of water. The filtrate was evaporated to dryness with 20 c.c. of concentrated nitric acid. The efficiency of the method was established by the very small blanks obtained on comparable known solutions of potassium iodide and sulphuric acid.

Analysis of the hydrogen peroxide mixtures was carried out as usual.

Experiment D. (*Theory, p.* 915.)—Air and sulphur dioxide were bubbled together for 4 days through 1 l. of distilled water at room temperature contained in a flask from which light was excluded. All excess of sulphur dioxide was removed by continuing the air current alone. The solution, now 0·1046*N* with respect to sulphuric acid, was treated with barium hydroxide in

TABLE I.

Dithionate formed by Iodine.

Details of expt.	$K_2S_2O_5$ used, g.	$BaSO_4$, g., from $K_2S_2O_6$ in $K_2S_2O_5$.	Total $BaSO_4$ from S_2O_6'', g.	$BaSO_4$ due to S_2O_6'' formed by iodine, g.	SO_2, %, oxidised to S_2O_6''.
SO_2 bubbled through 0·3*N*-iodine until in bare excess; then 2 c.c. *N*/10-iodine added	Equiv. to about 1·07	—	0·0038	0·0038	0·17
KI_3 added all at once to $K_2S_2O_5$ dissolved in 80 c.c. H_2O	1·02	0·0090	0·0120	0·0030	0·14
Ditto, but with 80 c.c. *N*-HCl	1·007	0·0089	0·0255	0·0166	0·77
Ditto, but with 80 c.c. 2*N*-HCl	1·01	0·0089	0·0215	0·0126	0·59
KI_3 added dropwise to $K_2S_2O_5$ in 80 c.c. *N*-HCl	1·02 *	0·0090	0·0188	0·0098	0·52
KI_3 added to 80 c.c. H_2O; solid $K_2S_2O_5$ then dropped in	1·011	0·0089	0·0188	0·0099	0·47
KI_3 acting on $K_2S_2O_5$ when ground in mortar with very little H_2O	0·995	0·0088	0·0187	0·0099	0·47
Similar to last expt. at first, then diluted to 100 c.c.	0·998	0·0088	0·0230	0·0142	0·68

* Some SO_2 was lost in the current of CO_2, so only about 0·90 g. was actually oxidised by iodine.

All but the last two experiments were done in a flask with a current of CO_2 passing all the time. The KI_3 solution used was sufficient to give a 0·3*N*-iodine solution whed diluted to 80 c.c. All water or acid used had been well boiled and cooled in CO_2.

Dithionate formed by Hydrogen Peroxide.

Solid $K_2S_2O_5$ added to 8 c.c. of 3*N*-H_2O_2 in 25 c.c. H_2O	1·059	0·0095	0·0117	0·0022	0·10
Solid $K_2S_2O_5$ added to 8 c.c. of 3*N*-H_2O_2; mixture cooled	1·108	0·0100	0·0192	0·0092	0·46
Solid $K_2S_2O_5$ added to 8 c.c. of 3·4*N*-H_2O_2; mixture cooled	1·258	0·0109	0·0360	0·0251	0·95
Solid $Na_2SO_3,7H_2O$ added to 7 c.c. of 3·4*N*-H_2O_2; mixture cooled	2·506	0·0014	0·0014	none	nil

the cold, and the barium sulphate filtered off next day. The filtrate was treated with potassium carbonate to convert the barium dithionate into the potassium salt, which is easier to isolate. The filtrate and washings from the barium carbonate were evaporated to a small bulk on the water-bath and then allowed to dry slowly at room temperature. The solid residue so obtained contained a good proportion of bright, well-formed, six-sided prisms, like those of authentic potassium dithionate preparations. After being washed on the pump with several small quantities of water and air-dried, the weight was 0·1034 g. The potassium dithionate lost in the wash waters was found to be 0·0363 g. as determined by the usual method (p. 923). The total yield, including that in the wash water, corresponded to 2·15% of the total sulphur dioxide oxidised.

The salt was heated in a hard-glass test-tube in a current of carbon dioxide, and the sulphur dioxide liberated was passed into *N*/10-iodine. The residue of potassium sulphate was then weighed, and the barium sulphate it yielded also determined. These three methods showed the purity of the potassium dithionate to be 93·23, 98·45, and 98·95% respectively.

Experiment E. (*Theory, pp.* 915, 916.)—The solution (200 c.c.) to be oxidised was contained in a Winchester-quart bottle fitted with tubes and taps so that samples could be driven up into a pipette by means of the pressure of oxygen from a cylinder. The oxygen pressure in the bottle underwent considerable fluctuation during the course of an experiment, but this would not appreciably affect the proportion of dithionate produced, and the rate of oxidation was not receiving particular attention. The bottles were mechanically shaken during the oxidation. After displacement of sulphur dioxide, sulphate and dithionate were estimated in the solution, free sulphurous acid or sulphite being estimated in a separate sample.

(i) *Oxidation of sulphurous acid by free oxygen.* Five different initial concentrations of sulphurous acid were used and in two cases oxidation was allowed to proceed nearly to completion. The results are in Table II.

(ii) Water was saturated with sulphur dioxide (3·65*N*) at room temperature, and a current of the gas and of oxygen passed through for four hours at such rates that the solution remained saturated with sulphur dioxide, excess of which was then removed by carbon dioxide. The

TABLE II.

Time, hrs., from start of expt.	Final SO_2, *N*.	H_2SO_4, *N*.	$BaSO_4$, g. from 10 c.c. $H_2S_2O_6$ soln.	Yield, %, of $H_2S_2O_6$.	Average concn., *N*, during time stated.	
					SO_2.	H_2SO_4.
72	0·188	0·211	0·0040	1·6	0·293	0·106
138	0·114	0·290	0·0059	1·7	0·255	0·145
210	0·0910	0·329	0·0068	1·7	0·245	0·164
7·5	0·567	0·0940	0·0027	2·4	0·614	0·047
29·5	0·449	0·226	0·0067	2·5	0·563	0·114
54	0·383	0·308	0·0092	2·5	0·537	0·154
97·5	0·317	0·405	0·0131	2·7	0·519	0·202
171	0·264	0·496	0·0162	2·7	0·512	0·248
72	0·425	0·478	0·0147	2·6	0·664	0·239
138	0·301	0·593	0·0191	2·7	0·598	0·296
25	0·986	0·404	0·0165	3·4	1·19	0·202
47	0·854	0·569	0·0235	3·4	1·14	0·285
72	0·753	0·680	0·0286	3·5	1·09	0·340
116	0·629	0·845	0·0327	3·3	1·05	0·422
190	0·555	0·976	0·0368	3·1	1·04	0·490
285	0·398	1·10	0·0396	3·0	0·946	0·550
96	1·26	1·07	0·0514	4·0	1·79	0·535

solution so obtained was 0·0155*N* with respect to sulphuric acid and contained dithionate equivalent to 6·8% of the sulphur dioxide oxidised. When the experiment was carried out in a waxed bottle protected from light, the yield of dithionate was 6·2%, with 0·0136*N*-sulphate. This yield is probably the highest obtainable from pure sulphur dioxide solutions.

(iii) *Oxidation of pyrosulphite in solution.* To allow for superficial oxidation of the sample of sodium pyrosulphite some of the solution was analysed as soon as all the solid had dissolved. Time was then allowed for about 20—30% oxidation to occur, and the solution again analysed. The mean of the two sulphur dioxide determinations gave the average concentration of pyrosulphite over the period of oxidation, and the differences between the two sulphate and dithionate estimations gave the quantities of sulphate and dithionate formed by oxidation in the solution. The results are in Table III.

TABLE III.

Expt.	Duration of oxidation, mins.	Diff. of $BaSO_4$ from sulphate, g.	Diff. of $BaSO_4$ from dithionate, g.	Mean concn. (*N*) of SO_2 ($N=M/2$).	Dithionate produced, % of SO_2 oxidised.
a	1560	0·1634	0·0059	0·205	3·5
b	95	0·0971	0·0052	0·507	5·1
c	120	0·5342	0·0360	0·924	6·3
d	105	0·4524	0·0332	2·01	6·8
e	840	0·7571	0·0574	1·86	7·1
f	115	0·5344	0·0431	2·95	7·5
g	120	0·4251	0·0368	4·13	8·0

The figures refer to a 25-c.c. sample for (a), and to 10 c.c. for other cases. In (e) air was used instead of oxygen.

Experiment F. (*Theory, p.* 916).—The solution (274 c.c.) was filtered from ammonium sulphate and sulphur (18·325 g.). The solution and sulphur washings were analysed separately.

Comp. of solution.
Total SO_4'' = 4·94*M*
H_2SO_4 = 1·04*M*
$(NH_4)_2SO_4$ = 3·90*M*
SO_3'' = 0·004*M*
S_3O_6'' = 0·00032*M*
S_2O_6'' = 0·339*M*

Total contents of bottle.
SO_4'' = 417·3 g. $BaSO_4$
S_2O_6'' = 57·6 g. $BaSO_4$

Experiment G. (*Theory, pp.* 915, 916, 919.)—Two tubes, (*a*) and (*b*), each contained 10 c.c. of ammonia (*d* 0·880) and 10 c.c. of water; the solutions were saturated with sulphur dioxide, the tubes sealed, and (*a*) exposed to diffuse light and (*b*) kept in a cupboard. The yellow solutions began to deposit sulphur after (*a*) 28 months and (*b*) 8 years. Reaction appeared to be complete after (*a*) 4 years 2 months and (*b*) 8 years 5 months, and the tubes were then opened and their contents analysed:

	Wt. of solid S, g.	Composition of solution (M).				
		H_2SO_3.	$(NH_4)_2SO_4$.	H_2SO_4.	$H_2S_3O_6$.	$H_2S_2O_6$.
(*a*)	1·575	0·52	3·41	1·55	0·004	—
(*b*)	1·522	0·62	3·48	1·35	0·075	0·016

Experiment H. (*Theory, p.* 917.)—(i) 250 G. of potassium dichromate, 2 l. of water, and 170 c.c. of concentrated sulphuric acid were added in stages, to prevent overheating, to 2 l. of saturated sulphur dioxide solution. The slight excess of gas was gently boiled off, and the solution allowed to evaporate to dryness at room temperature. After the chrome alum had been dissolved in cold water, both chromium and sulphate were removed by basification with baryta solution, and the liquid was filtered and concentrated to about 1 l.; considerable sulphate still present was removed by further addition of baryta, and on concentration of the filtrate and cooling, a fair crop of six-sided prismatic crystals of potassium dithionate mixed with a little carbonate separated. On recrystallisation from hot water, 5·43 g. of the dithionate were obtained [0·2538 g. gave 0·1850 g. K_2SO_4 on ignition (Calc., 0·1856 g.); 0·1050 g. after oxidation by HNO_3 gave 0·2045 g. $BaSO_4$ (Calc., 0·2055 g.)]. The dithionate remaining in the mother-liquors was estimated gravimetrically, and the total yield found to be 8·68 g., corresponding to 2·82% of the sulphur dioxide oxidised.

If the freshly reduced green solution is precipitated directly with barium hydroxide essentially the same result is obtained.

(ii) A concentrated (3·07N) sulphur dioxide solution was exactly oxidised by 36·51 g. of potassium permanganate in 1 l. of water, both solutions being air-free. After removal of manganese and sulphate with baryta, 12·7 g. of pure potassium dithionate were isolated, and that found by analysis in the mother-liquors corresponded to 0·7 g.; hence, the total yield of dithionate was 17·7% of the sulphur dioxide oxidised.

Experiment I. (*Theory, p.* 917.)—Using approximately $N/10$-solutions of sulphurous acid, iodine, and sodium thiosulphate, and the experimental procedure described by Bassett (*loc. cit.*), it was found that when unboiled water was added to the sulphurous acid, practically no oxidation of the latter by the dissolved oxygen occurred: a mixture of 25 c.c. of sulphurous acid and 275 c.c. of water left for ½ hour before addition of the iodine reduced only 0·15 c.c. less iodine than if no water was added, whereas 275 c.c. of water saturated with air at atmospheric pressure at 20° contain dissolved oxygen equivalent to 3·06 c.c. of $N/10$-iodine.

When 50 c.c. of sulphurous acid, 250 c.c. of water, and 100 c.c. of 4N-sulphuric acid were treated with 25 c.c. of $N/10$-potassium dichromate (all unboiled), it was found, on estimation of the excess of sulphurous acid with iodine and thiosulphate, that 2·5 c.c. less iodine were reduced by the excess than in a precisely similar experiment in which the added water and sulphuric acid had been first boiled and then cooled in carbon dioxide. The greater part of the dissolved oxygen had evidently been activated by the dichromate reaction. The activation by permanganate is even greater, for in a similar pair of experiments with $N/10$-potassium permanganate, the dissolved oxygen which had been activated was equivalent to 3·28 c.c. of $N/10$-iodine.

In order to reduce the effect of dissolved oxygen to a minimum, it was necessary to boil solutions for at least 10 minutes and then cool them in a current of carbon dioxide or nitrogen.

Experiment J. (*Theory, p.* 917.)—In the following volumetric experiments the various solutions were added in the order in which they are shown in Table IV from left to right. When the volume given in col. 4 is greater than the sum of those in cols. 1 and 2, well-boiled water cooled in carbon dioxide had been added as well. When liquid sulphur dioxide was used, the gas was passed into the volume of liquid shown in col. 4. Addition of hydrochloric instead of sulphuric acid leads to low yields of dithionate owing to coupled oxidation of chloride ion.

Experiment K. (*Theory, p.* 917.)—To 25 c.c. of 3·58N-sulphurous acid (freshly prepared), diluted to known volumes with air-free water, were gradually added 62·34 c.c. of N-potassium dichromate, the mixture being kept cold. Excess baryta was then added, and after several days the precipitated chromium hydroxide and barium sulphate and sulphite were filtered off and washed. Excess of sulphite was removed by heating after slight acidification, or in the case of Expt. (*e*) by addition of $N/10$-iodine, and dithionate determined after removal of any sulphate with barium chloride. Two series of experiments with potassium permanganate were carried out essentially as above, but since the exact amount necessary to oxidise all the sulphite could be seen, this was added in each case. Both series of results are given in Table V.

TABLE IV.

Experiments with (i) $K_2Cr_2O_7$ *and* (ii) $KMnO_4$.

	$4N$-H_2SO_4 used, c.c.	H_2SO_3 used, c.c.	H_2SO_3 used, normality.	Total vol., c.c., before adding $K_2Cr_2O_7$ or $KMnO_4$.	$K_2Cr_2O_7$ or $KMnO_4$ used, c.c.	$K_2Cr_2O_7$ or $KMnO_4$ used, normality.	Equiv. H_2SO_3 oxidised per equiv. $K_2Cr_2O_7$ or $KMnO_4$.	% of oxidised SO_2 yielding S_2O_6''.
(i)	100	50	0·0980	150	25·05	0·0998	1·024	4·7
	100	50	0·0979	1000	25·05	0·0998	1·026	5·1
	0	50	0·0964	50	25·05	0·0998	1·029	5·6
	0	50	0·0964	1000	25·05	0·0998	1·030	5·8
	0	50	0·847	50	25·05	1·003	1·023	4·5
	0	50	0·853	950	25·05	1·003	1·020	3·9
		Liquid, g.	= c.c. N.					
	50	1·4348	44·84	490	25·07	1·0	1·021	4·1
	50	1·0614	33·16	412	25·07	1·0	1·019	3·7
	0	1·2683	39·64	490	25·07	1·0	1·020	3·9
	50 *	1·0320	32·25	—	25·07	1·0	1·024	4·7
(ii)		c.c.	normality.					
	50	50	0·1048	100	25·05	0·0993	1·094	17·2
	0	50	0·0925	1000	25·07	0·0973	1·115	20·6
	50	50	0·8478	100	25·05	0·9945	1·084	15·5
	50	50	0·8478	1000	25·05	0·9945	1·075	14·0
	50	50	0·8466	100	25·05	0·9945	1·105	19·0
	0	50	0·8532	50	25·05	0·9945	1·099	18·0
	0	50	0·8532	1000	25·05	0·9945	1·085	15·7
	0 *	50	0·0926	—	25·07	0·0973	1·107	19·3
		Liquid, g.	= c.c. N.					
	50	1·7807	55·65	100	50	0·9815	1·088	16·2
	50	1·2675	39·6	490	25·07	0·9815	1·091	16·6
	100 †	2·2955	71·75	—	50	0·9945	1·110	19·8

* In these cases the H_2SO_3 was added to the $K_2Cr_2O_7$ (or $KMnO_4$) and H_2SO_4.

† This experiment does not agree with Carrière and Liauté's statement (*Compt. rend.*, 1933, **196,** 933) that only sulphate is formed when sulphurous acid is added to excess $KMnO_4$ which is more than 2·75N with respect to the H_2SO_4. In this case the SO_2 was passed into the acidified $KMnO_4$.

TABLE V.

Expt.	H_2SO_3 used, c.c.	H_2SO_3 used, normality.	Vol. diluted to c.c.	Temp.	Equivs. H_2SO_3 oxidised per equiv. $K_2Cr_2O_7$ or $KMnO_4$.	% of oxidised SO_2 yielding S_2O_6''.
			Oxidation by N-$K_2Cr_2O_7$.			
	25	3·58	25	20°	1·020	3·9
	25	3·58	100	16	1·021	4·1
	25	3·58	100	32	1·021	4·1
(*e*)	25	3·58	1000	16	1·021	4·1
			Oxidation by 0·581N-$KMnO_4$.			
	10	2·4	45	20—32	1·084	15·5
	25	2·4	250	20	1·084	15·5
	10	2·4	500	22	1·087	16·0
	10	2·4	45	40	1·084	15·5
(*a*)	5	2·4	20	room temp.	1·094	17·2
(*b*)	5	2·4	20		1·093	17·0
(*c*)	5	2·4	100		1·080	14·8
(*d*)	5	2·4	100		1·093	17·0

In experiments (*a*) and (*c*), the permanganate was added slowly with vigorous stirring and practically no trace of manganese dioxide was seen during the reaction, but in experiments (*b*) and (*d*) addition was intermittent with little stirring, and much dioxide was seen as an intermediate stage except near the beginning of the reaction. In each of the first four experiments with permanganate, some dioxide appeared. The appearance or non-appearance of this oxide evidently makes no difference to the course of the oxidation.

Oxidation of solid potassium pyrosulphite by excess permanganate. (*a*) 1·0008 G. of well-scraped pyrosulphite crystals were added to a mixture of 40 c.c. of N-potassium permanganate and 4·2 c.c. of concentrated sulphuric acid, excess of permanganate was destroyed by warming with a little concentrated hydrochloric acid, and the manganese dioxide filtered off and well washed. The dithionate in the filtrate corresponded to a yield of 18·85%.

(*b*) In a similar experiment, but without addition of sulphuric acid, 24·1% of the pyrosulphite was oxidised to dithionate.

Experiment L. (*Theory, p.* 922.)—Equal volumes of sulphurous acid (approx. 0·1*N*) were placed in two Winchester-quart bottles (previously used for hydrochloric acid), and to one, *A*, was added sufficient methylene-blue to make the solution 0·0013*M* with respect to it (0·03 g. in 200 c.c.). The air was displaced from the bottles by oxygen, and they were shaken mechanically; after suitable intervals of time, 10-c.c. samples were removed from each bottle, and the sulphuric acid estimated after displacement of sulphur dioxide by a current of carbon dioxide. The results are given in Table VI(*a*).

After the completion of the experiment the bottles were well rinsed out with cold water, and the experiment was repeated with the bottles interchanged. Very little oxidation took place in either bottle during the first 6 days, but bottle *A* then seemed to have regained its normal activity. The results are shown in Table VI(*b*).

Table VI.

	(*a*). BaSO$_4$, g., from 10 c.c. solution.			(*b*). BaSO$_4$, g., from 10 c.c. solution.	
Time (days).	Bottle *A*.	Bottle *B*.	Time (days).	Bottle *A*.	Bottle *B*.
2	0·0031	0·0155	3	0·0037	0·0033
4¼	0·0030	0·0422	6	0·0073	0·0040
6¼	0·0029	0·0615	13	0·0540	0·0070
9	0·0052	0·0822	17	0·0671	—
13	0·0063	0·0970	23	0·0832	0·0109
16	0·0066	0·1073	32	0·0972	0·0146
21	0·0092	0·1211			

Experiment M. (*Theory, p.* 922.)—In precisely the same way as in Expt. L, the rate of oxidation in absence of methylene-blue in a bottle which had been thoroughly lined with paraffin wax was found to be just about the same as in a clean unwaxed one, about 75% of the sulphurous acid being oxidised after 9 days' shaking.

When the sulphurous acid (0·105*N*) in the waxed bottle was made 0·0013*N* with respect to methylene-blue, only 5% of it had been oxidised after 7 days and 11% after 25 days. After the same waxed bottle had been well rinsed, a fresh 0·1*N*-sulphurous acid solution, but without any added methylene-blue, was shaken with oxygen as before, but the rate of oxidation remained at the same low level as when methylene-blue had been added, and no signs of recovery in the rate of oxidation were noted even after 26 days.

Summary.

1. Some of the sources of error in the determination of dithionate have been examined.
2. It is shown that the hydrolytic decomposition of dithionic acid is not reversible.
3. The oxidation of sulphurous acid and of sulphites by chlorine, iodine, hydrogen peroxide, oxygen, and chromic and permanganic acid has been examined.
4. Only very small amounts of dithionic acid are formed by the first three reagents, and that only under acid conditions.
5. Oxygen yields dithionate in amounts which depend upon the sulphite concentration and acidity and may be large.
6. The crusts which slowly form on solid alkali pyrosulphites in the air consist of a mixture of sulphate and dithionate containing about 25% of the latter. The oxidised material which forms on the solid "neutral" alkali sulphite contains the merest trace of dithionate.
7. Of the sulphurous acid oxidised by chromic and permanganic acids, about 4% and 19% respectively yields dithionic acid under all conditions of concentration and acidity.
8. The dithionate produced in the oxygen and chromic acid reactions was separated and identified as the potassium salt.
9. No dithionate appears to be formed during the photochemical decomposition of sulphurous acid into sulphuric acid and sulphur, but when the same decomposition occurs in the dark a small amount of dithionate is perhaps formed.

10. It is considered that the free sulphite ion is always oxidised to sulphate.

11. Dithionate is formed in at least four different ways : (*a*) Chlorine, iodine, hydrogen peroxide, oxygen, and similar oxidising agents produce it by the oxidation of pyrosulphite, not of normal sulphite; all of these oxidations occur with great rapidity except that by oxygen, which follows a chain mechanism. (*b*) Metal ions easily reducible to a lower valency stage, or to metal, yield dithionate as a result of complex-ion formation with sulphite ions, followed by self-oxidation and -reduction of the complex; the proportion of dithionate formed in these cases depends almost solely upon the nature of the metal and in certain cases it is possible for the complex-ion mechanism to allow of oxidation to dithionate in alkaline solution. (*c*) Chromic and permanganic acids produce dithionate by oxidation of neutral sulphur dioxide molecules; this is a result of self-oxidation and -reduction of anionic complexes of the heteropoly-acid type. The proportion of dithionate formed in these cases also depends almost solely upon the metal.

12. The mechanism of the electrolytic formation of dithionate is discussed, and it is considered to be due to the simple electrochemical process $2SO_3'' = (2SO_3' + 2e) = S_2O_6'' + 2e$. This is the fourth way referred to in **11**.

13. It is concluded that the reduction of permanganate by sulphite in alkaline solution, since only sulphate is formed, does not proceed by the complex-ion mechanism but by one in which the successive reduction products $MnO_4' \longrightarrow MnO_4'' \longrightarrow MnO_4''''$ are formed, the last of which breaks down to dioxide, which is precipitated. This reduction mechanism may apply to other oxidations by permanganate in alkaline solution.

14. It is shown that methylene-blue inhibits the atmospheric oxidation of sulphurous acid, but that it is itself slowly oxidised with gradual removal of the inhibiting action.

15. The oxidation results give no evidence whatever for the existence of any sulphurous–sulphonic equilibrium in sulphurous acid solutions.

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