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XXX.—The Constitution of some Non-saturated Oxygenous Salts, and the Reaction of Phosphorus Oxychloride with Sulphites and Nitrites.

#### By Edward Divers, M.D.

THE object of the present paper is to show that non-saturated oxygenous salts differ from those which are saturated, not in the manner in which they are universally represented as doing—namely, in having their chlorous elements of a lower than their maximum valency—but in being less oxylic than the saturated salts of the same element, or, in the case of metallic salts of monobasic acids, not oxylic at all.

### Sulphites-no Evidence that they are Dioxylic.

Two views have been held concerning the constitution of sulphites as salts. According to the one, they are half haloïd salts, half oxylic, as represented by the formula  $\begin{array}{c} Ag \\ AgO \end{array} > SO_2$ . This view was proposed by Odling very many years ago, but has long since been given up by him for the other.\* According to this view, the constitution of

<sup>\*</sup> It was also held by Strecker and others, and in England the late Henry Watts VOL. XLVII. Q

sulphites is the same as that of sulphonates, and may therefore be for brevity called the *sulphonic* constitution.

On the other view, sulphites are dioxylic, as represented by the formula (AgO)<sub>2</sub>SO. This view is now generally accepted, in spite of several well-known reactions not in harmony with it.

The reasons for this acceptance seem to be mainly two—one that the sulphites are so much less stable than the sulphonates; the other, the conviction that all oxygen salts are oxylic salts, including sulphites, considered to have been proved such by experiments with phosphorus pentachloride and oxychloride.\* Of these reasons, I shall discuss the latter first, so far at least as it rests on experimental evidence in the case of the salts in question.

Action of Phosphorus Pentachloride on Sulphites.—From the time of the successful application of the chlorides of phosphorus by Gerhardt, Cahours, and others, in the investigation of the constitution of organic acids, the adaptability of these reagents for a similar purpose in inorganic chemistry has been assumed, but has been only very imperfectly established by experiment. However, among the salts examined are the sulphites, and these we learn have yielded results with both the pentachloride and the oxychloride of phosphorus, leading to the conclusion that sulphites are dioxylic compounds of the radicle thionyl, as represented by the formula for silver sulphite,  $(AgO)_2SO$ .

On the authority of Carius,<sup>†</sup> phosphorus pentachloride heated with a sulphite yields thionyl chloride,  $Cl_2SO$ . I have not thought it necessary to verify this statement, as I see no grounds for doubting its accuracy. I have only to show that this formation of thionyl chloride has no significance whatever in determining the constitution of a sulphite. The thionyl chloride comes assuredly from a secondary reaction after the decomposition of the sulphite has been effected. To insist that it does not would require us to admit that an organic sulphonate is also a thionyl compound. For when the pentachloride is heated at  $120^{\circ}$  with sodium ethanesulphonate, thionyl chloride is the sulphur-product. But, as Carius, who observed this, has shown that ethanesulphonic chloride is normally formed at first—

in his last edition of *Fownes' Organic Chemistry*, adopted it, suggesting, however, the existence of sulphites of both one and the other constitution. Michaelis and Landmann also give the sulphonic constitution to metallic sulphites, while leaving to selenites the dioxylic one. So also, in one place, Takamatsu and Smith use the sulphonic formula in their paper on pentathionic acid.

\* Another reason is probably to be found in the old-established notion that oxygen salts are always built up of an oxidised basylous and an oxidised chlorous radicle.

+ Roscoe and Schorlemmer's *Treatise*. The correctness of this reference to Carius is doubtful. See next note.

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#### NON-SATURATED OXYGENOUS SALTS.

# $NaOEtSO_2 + PCl_5 = ClEtSO_2 + NaCl + Cl_3PO$ ,

and then spontaneously decomposes—slowly in the cold, more rapidly when heated—into sulphur dioxide and chlorethane, and has further shown that phosphorus pentachloride readily converts sulphur dioxide into thionyl chloride, the question of the sulphonic constitution is not touched by this derivation of thionyl chloride from a sulphonate. The corresponding production of thionyl chloride, observed by Barbaglia and Kekulé, on heating benzenesulphonic chloride with phosphorus pentachloride at 200°, should receive a similar explanation rather than the one proposed by Michaelis, in which sulphuryl chloride appears as a transition-body.

If we now conceive a sulphite as having the constitution, not of a dioxylic salt, but of a sulphonate, its reaction with phosphorus pentachloride will give as a transition-product a metallic chlorosulphonate, say  $ClNaSO_2$ , and this will certainly at once be decomposed into metallic chloride and sulphur dioxide; the latter will then be acted on by more pentachloride and changed into thionyl chloride.

Action of Phosphorus Oxychloride on Sulphites .- A statement occurs in Odling's Manual of Chemistry that thionyl chloride is produced by the action of oxychloride of phosphorus on metallic sulphites, and in Watts's Dictionary Carins is given as the authority for this statement.\* The objection to the use of phosphorus pentachloride as a test of the constitution of an acid is that its action may extend not merely to the oxylic oxygen but also to the oxygen of the radicle, or that which is non-oxylic. This objection cannot be made against phosphorus oxychloride, which apparently can be charged by no possibility with confounding the two kinds of combined oxygen, except in the very rare case, as with boron oxide at high temperatures, of its reversion to the pentoxide and pentachloride from which it has, or may have, been formed. It cannot be denied, therefore, that the production of thionyl chloride from a sulphite by the action of phosphorus oxychloride would prove the constitution of a sulphite to be that of a thionyl compound. Recognising this, and at the same time seeing the weight of evidence there is that sulphites

\* Annalen, 70, 297. Here, in Japan, I cannot refer to the Annalen to verify this statement. But although the first volume of Liebig and Kopp's Jahresbericht gives statements from the earliest pages of vol. 70 of the Annalen, it contains no mention of Carius, whose name does not appear in the Jahresbericht until some years later. In the Annalen, 106, 307, he gives the action of phosphorus pentachloride, not of oxychloride, on a sulphate. Possibly, therefore, Carius is credited with this statement by mistake. [A mistake has been made. The paper referred to is entitled: "Ueber Schwefigsaures Phosphorchlorid; von P. Kremers," and describes the action of  $PCl_5$  on  $SO_2$ , the product examined being it is now obvious a mixture of  $SOCl_2$  and  $POCl_3$ .—H. E. A.] have not this constitution, I had some experiments made by Mr. Tetsukichi Shimidzu, M.E., who has kindly given every care to the matter, including that of preparing the oxychloride and the sulphites.

The sulphites selected were those of lead, calcium, and sodium. Trials were repeatedly made with each of these sulphites and the oxychloride, but in no instance could any thionyl chloride or other oxychloride of sulphur be obtained. The sulphite remained for the most part unchanged, but was partly converted into sulphur dioxide, together with chloride and phosphate of the metal. Most of the unaltered phosphorus oxychloride which distilled over condensed in the well-cooled receiver, but a little of it escaped as vapour along with the sulphur dioxide. When treated with water, this gas gave, therefore, a chlorine reaction, but it also gave a phosphoric acid reaction. The condensed phosphorus oxychloride appeared to be pure, and gave neither sulphur dioxide nor sulphuric acid with water. As thionyl chloride boils to 82°, it would, if formed, have been present in this liquid. The reaction which takes place is no doubt as follows :---

$$3Na(NaO)SO_2 + Cl_3PO = 3NaCl + (NaO)_3PO + 3SO_2$$

So far, then, from proving the dioxylic structure of sulphites, the action of oxychloride of phosphorus furnishes, perhaps, direct evidences of their sulphonic character. It is probable, however, that thoroughly dry and pure sulphites are not acted on at all by pure phosphorus oxychloride.

# Sulphites-Evidence that they are not Dioxylic.

Action of Heat on Sulphites. — It has been known for a very long time that sulphites yield sulphides and sulphates when heated. Quite recently, Geuther has materially added to our knowledge of the change which then takes place, by examining the effect of heat on potassium hydrogen sulphite.\* He finds that at 190° this salt gives off water and sulphur dioxide, and leaves a mixture of two molecular proportions of sulphate to one of thiosulphate. The explanation of this appearance of thiosulphate is clearly that the acid sulphite becomes normal sulphite, sulphur dioxide, and water, in the first place, and that then one molecule of sulphur dioxide reacts with three molecules of normal sulphite to form two molecules of sulphite and one of thiosulphate, thus :—

1st. 
$$6 \text{KHSO}_3 = 3 \text{K}_2 \text{SO}_3 + 3 \text{SO}_2 + 3 \text{OH}_2$$
.  
2nd.  $3 \text{K}_2 \text{SO}_3 + \text{SO}_2 = 2 \text{K}_2 \text{SO}_4 + \text{K}_2 \text{S}_2 \text{O}_3$ .

As Geuther points out, the thiosulphate when strongly heated yields

\* Pyrosulphite with water of crystallisation (Berthelot).

sulphate and the sulphide hitherto recognised as a product of the operation.

Taking into consideration the conclusive evidence there is of thiosulphate having half its sulphur in place of half the oxylic oxygen of a sulphate, the formation of either thiosulphate or sulphide from a sulphite by heat points unmistakably to a constitution for sulphites in which the metallic radicle is partly in direct union with the sulphur, since with a dioxylic structure—that is, with both metal and sulphur oxidised—no mode of reaction is open by which a sulphide could be formed.\*

Experiments on the Decomposition of Sulphur Dioxide by Alkali Sulphites.—Wishing to test the accuracy of the assumption I have made in the preceding paragraph and the foot-note to it, that sulphur dioxide is resolved into its elements by hot sulphites, I have got Mr. Shimidzu to heat dry sodium sulphite in dry sulphur dioxide. His results are interesting and entirely confirmatory of my assumption.

The sulphite used, after being dried in the air at about 90°, was found to contain a little sulphate, and to dissolve in water to a clear solution, remaining so after acidification. Some of this salt was kept for half an hour at a temperature of 190°, and again tested. It was unchanged. Other portions were then heated in sulphur dioxide for ten minutes at 190°, air being excluded and the sulphur dioxide dry. Temperatures near 190° were employed, because at this temperature Geuther obtained the sulphate and thiosulphate.

A small sublimate of sulphur was thus obtained, and besides, sufficient sulphur remained intermixed with the sulphite to render its solution milky. A little thiosulphate was also formed, and very distinctly more sulphate than the small quantity present before the experiment.

From this it is clear, first, that alkali sulphite moderately heated decomposes sulphur dioxide, taking its oxygen to form sulphate, and

\* Geuther states that the pyrosulphite  $(K_2S_2O_5)$  also yields this sulphate. But this is opposed to Berthelot's precise statement that the pyrosulphite yields only sulphate, sulphur dioxide, and sulphur, since if this ulphate were formed, it would leave sulphide. Berthelot's finding seems the more probable :—

$$2K_2S_2O_5 = 2K_2SO_4 + SO_2 + S,$$

one molecule of the sulphur dioxide yielding free sulphur, and giving up its two atoms of oxygen to two molecules of normal potassium sulphite. The normal sulphite if heated strongly also yields sulphate and polysulphide, a fact recently confirmed by Geuther. Here, of necessity, alkali oxide must be formed, although not mentioned, probably combined with the material of the crucible. In this case too, therefore, we have sulphur dioxide at our disposal to account for the change by its reaction with undecomposed sulphite. rejecting the sulphur,\* when the dioxide is in large excess; and secondly, that it also takes the sulphur to form thiosulphate when the sulphur dioxide is present only in limited quantity.

The experiments, which were several times repeated, were not of long duration, as in that case errors might have arisen through some action of entering air, or some very slow dissociation of the sulphite, and thus the value of the results would have been lessened. We relied on the characteristic silver test in proving the presence of thiosulphate.

The Quinine Test for Non-oxylic Salts.—Stokes (this Journal, 22, 174) has pointed out that a haloïd or non-oxylic salt not only does not form a strongly fluorescing salt with quinine, but even quenches the fluorescence of an oxylic salt of that base. He did not examine sulphites, but Mr. Shimidzu and I find that a solution either of a sulphite or of sulphur dioxide, added to a sulphuric acid solution of quinine, at once destroys the fluorescence, and therefore, to the extent to which this test is trustworthy, proves that it contains a (partly) non-oxylic acid.

Double Sulphites of Silver.—Silver sulphite dissolves in alkali sulphites to form double sulphites. Alkali sulphites freely dissolve even silver chloride. Now, since silver does not form double salts of acids which are exclusively oxylic,<sup>+</sup> and very readily forms double salts of haloïd acids, this property of silver sulphite is evidence of its being (partly) non-oxylic.

Conversion of certain other Salts to Sulphites by Sodium, and of Sulphites to other Salts by Chlorine or Iodine.—The now well-known results obtained by Otto, Spring, and others, by the action of sodium-amalgam on alkali hyposulphates, trithionates, and thiosulphates, only require to be formulated in order to show undeniably that sulphites are not dioxylic :—

Hyposulphate. Sulphite.  $(NaSO_3)_2 + 2Na = 2(NaSO_3)Na.$ Trithionate.  $(NaSO_3)_2S + 4Na = 2(NaSO_3)Na + Na_2S.$ Thiosulphate.  $(NaSO_3)SNa + 2Na = (NaSO_3)Na + NaSNa.$ 

To these I may add the reaction observed by Mr. Haga and myself (p. 203) :=

\* Sulphur dioxide, in like manner, is deoxidised by hypophosphorous and phosphorous acids (Ponndorf), and by phosphenylous acid (Michaelis and Ananoff).

<sup>+ [</sup>See, however, Russell and Maskelyne, Proc. Roy. Soc. (1877), 26, 357.-H. E. A.]

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Nitrososulphate. Hyponitrite.  $(NaSO_3)N_2O_2Na + 2Na = (NaSO_3)Na + Na(N_2O_2)Na.$ 

Spring's observations on the effects of sulphur chloride and of iodine on sulphites alone, and these salts in admixture with sulphides and with thiosulphates, are equally conclusive :---

Sulphite. Trithionate.  $2(NaSO_3)Na + SCl_2 = (NaSO_3)_2S + 2NaCl.$   $(NaSO_3)Na + NaSNa + I_2 = (NaSO_3)SNa + 2NaI.$  $(NaSO_3)Na + (NaSO_3)SNa + I_2 = (NaSO_3)_2S + 2NaI.$ 

The Interrelations of Sulphites with Sulphonates and Sulphinates.— There are no facts more decisive as to the non-dioxylic structure of sulphites than those I have now to adduce, so familiar to chemists. The conversion of an organic sulphonate into a metallic sulphite, by fusing it with alkali hydroxide, is one of its earliest known reactions :—

 $(NaSO_3)Ph + NaOH = (NaSO_3)Na + PhOH.$ 

In order to avoid the use of this direct expression of the change, and to write a sulphite as a thionyl compound, we must leave facts for fancy, and regard alkali hydroxide as *deoxidising* an acid radicle, that is, sulphuryl to thionyl.

As the complement of this reaction of a sulphonate, there is Strecker's reaction of a sulphite, as modified by Hemilian, in which in aqueous solution the sulphite becomes sulphonate :—

 $(AmSO_3)Am + PhCl = (AmSO_3)Ph + AmCl.$ 

Either this equation represents the change, or the remarkable assumption must be made that phenyl chloride can bring about the oxidation of thionyl to sulphuryl.

While sulphonates can be hydrolysed to sulphuric acid (Armstrong and Miller), one sulphite at least can be similarly hydrolysed, the metal of which is more stable when free than are its oxygenous compounds. Compare silver sulphite with benzenesulphonic acid :---

$$\begin{array}{rl} \mathrm{HPhSO}_3 &+ \mathrm{H}_2\mathrm{O} = \mathrm{PhH} &+ \mathrm{H}_2\mathrm{SO}_4 \\ \mathrm{AgAgSO}_3 &+ \mathrm{H}_2\mathrm{O} = \mathrm{AgAg} + \mathrm{H}_2\mathrm{SO}_4. \end{array}$$

Yet again does the conviction force itself upon one that sulphites, sulphonates, and sulphates have all one radicle, sulphuryl. For just as a sulphonate is related to a sulphate in Armstrong and Miller's

reaction, so is a sulphinate related to a sulphite in the reaction observed by Otto and Ostrop to take place at 250-300° between sodium benzenesulphinate and sodium hydroxide :---

$$Ph(SO_2Na) + (NaO)H = NaO(SO_2Na) + PhH.$$

It may be added that as in the group  $-SO_2Na$  the sodium is replaceable by chlorine, its constitution cannot be -(SO)ONa; so that the above reaction shows the constitution of a sulphite to be  $NaO(SO_2)Na$  no less clearly than does the reciprocal convertibility of sulphites and sulphonates.

# Sulphites—their Relative Instability to be Accounted for by the Presence of their Unoxidised Metallic Radicle.

As I stated at the beginning of this paper, one of the reasons which have prevented the adoption of the same constitution for sulphites as for sulphates, is the instability and oxidisability of the former, as compared with the stability and non-oxidisability of the sulphonates. Recent experiments by Prinz extend this difference; for he has found that a sulphonate, unlike a sulphite, does not combine with sulphur.

The different behaviour of sulphites and sulphonates is, however, much more probably due to difference in composition than to difference in constitution. Sulphites have half their metal united directly to the sulphur of sulphuryl, and this part of the metallic radicle it is which readily combines with unoxidised sulphur, with oxygen, or with nitric oxide. Sulphonates, on the other hand, are not oxidisable because they have hydrocarbon in place of the unoxidised part of the metal of sulphites, and this hydrocarbon does not reject direct union with sulphuryl for that with oxygen or sulphur. Again, potassium ethanesulphinate is oxidisable to sulphonate, without—and this is admitted, be it remembered—change of the sulphuryl, but by the interposition of oxygen between the metal and the sulphur, as thus represented :—

$$K(SO_2Et) + O = KO(SO_2Et),$$

whilst sulphones, which have the same constitution as sulphinates, are not thus oxidisable, because instead of a metallic radicle they have a second hydrocarbon radicle. Ethyl sulphides do not, like alkali sulphides, oxidise in the air. It is just their sulphonic constitution, then, which makes sulphites, like soluble sulphides,\* oxidisable and unstable.

\* In a recent communication to the Society on the origin of thiosulphates, I have given experimental evidence that in the atmospheric oxidation of soluble sulphides it is the hydrogen or basylous radicle which oxidises, not the sulphur.

Thus interpreting the significance of the oxidisability of sulphites, we find evidence of the existence of free sulphurous acid (hydrogen sulphite) in moist or dissolved sulphur dioxide, because this is readily oxidisable whilst dry sulphur dioxide is not, except by active oxygen. When moist it has become partly changed into sulphurous acid of the formula  $\frac{HO}{H}$ >SO<sub>2</sub>, and contains, therefore, unoxidised hydrogen. Its slow oxidation to hyposulphuric acid (Jacquelain) is still more conclusive :—

$$2(SO_3H)H + O = (SO_3H)_2 + H_2O.$$

Where the metallic radicle, as in the case of silver sulphite, is not an oxidisable one, the instability of the sulphite is of another order, one that has been explained on a previous page.

## Sulphites not being Dioxylic, there is no Evidence that Sulphur is Sexvalent towards Oxygen.

That sulphur is bivalent when not directly combined with a more chlorous element, such as oxygen or chlorine, is universally admitted. That it is quadrivalent in some, if not all of its compounds, when it is so combined, is shown by the existence of the sulphines, and by the evidence of the existence of sulphur tetrachloride at low temperatures. Pointing quite as clearly to the same conclusion is the fact of the formation of thionyl chloride, effected by Michaelis and Schifferdecker, by the action of sulphur trioxide on sulphur tetrachloride (sulphur chloride and chlorine in a freezing mixture).

But the removal, here attempted to be made, of the distinction hitherto conceived to exist between the constitution of sulphites and sulphonates, taken in connection with the fact of the intimate relations of sulphates to sulphonates, raises the question whether sulphur is ever sexvalent towards oxygen,\* as commonly supposed, and not always quadrivalent.

It is certainly a fact significant of the weakness of the case for sulphur being ever sexvalent, that for so many years Pelouze's nitrosulphate, a body of undetermined and apparently unique constitution, should have done duty as the stock illustration of this relation of sulphur. It has done so, of course, only for the want of a better.

Berthelot finds the peroxide of sulphur discovered by him to have the formula  $S_2O_7$ . The existence of such a compound, although not

<sup>\*</sup> Dehu's compounds of ethylene bromide with the sulphides of ethylene and of ethyl, and Dobbin and Masson's recently described halogen compounds of trimethylsulphine seem to show that sulphur can be sexualent in presence of hydrocarbon radicles.

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necessarily inconsistent with the quadrivalency of sulphur, must nevertheless give a certain degree of improbability to it. But then there is the strongest reason furnished, both by analogy and by the general character of sulphur compounds, to receive with doubt any evidence of the existence of a peroxide of sulphur having an odd number of oxygen-atoms along with a symmetrical constitution. An oxide with the formula  $S_2O_3$ , probably  $S_4O_6$ , is indeed known, but it is certainly not a symmetrical oxide, or compound of equally oxidised sulphur-atoms. Berthelot gives S<sub>2</sub>O<sub>5</sub> in his list of formulated oxides, but this only represents the group seen in the formulæ of hyposulphates and pyrosulphites when written K<sub>2</sub>O,S<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>,S<sub>2</sub>O<sub>5</sub>, respec-On the other hand, evidence of the existence of a peroxide, tively. SO<sub>4</sub>, having 4 atoms of oxygen to the atom of sulphur, would be welcome as matching the sulphur, selenium, and tellurium compounds with sulphur trioxide. Moved by these reasons, then, we might fairly be led to entertain doubts as to the trustworthiness of the analytical results obtained by Berthelot, did he not express confidence in their accuracy, especially if we consider the difficulty of bringing such a substance in contact with reducing agents without thereby causing oxygen to be set free. It does not, however, seem too much to assume that, since the peroxide is constantly losing oxygen when prepared, and is being decomposed during its preparation by the very means employed to make it, as in the case of ozone, it will, if only  $S_2O_7$ when single and perfect, scarcely yield the full 7 atoms of oxygen as the samples of it analysed were found to do. I may therefore be allowed to suggest that, in spite of all his skill, even such a veteran chemist as Berthelot may have only succeeded in preparing and analysing the peroxide when mixed with nearly half its weight of trioxide, and thus have found only 7 atoms instead of 8 of oxygen to every 2 atoms of sulphur.

The octosulphates and lesser polysulphates quite recently described by R. Weber belong apparently, as chemical compounds, to the same category as hydrates, and do not, therefore, concern my present thesis.

Returning now to a consideration of the nitrosulphates as examples of compounds of sexvalent sulphur. To make them serve as such, they are written  $S^{vl}O(OK)_2(NO)_2$ . But as they are formed from sulphites by adding nitric oxide, just as sulphates are formed by adding oxygen to sulphites, thiosulphates by adding sulphur, and pyrosulphites by adding sulphur dioxide\* (even in presence of water), the four salts may be written uniformly, thus :—

<sup>\*</sup> The radicle  $SO_2$  can enter here between the metal and the  $(SO_3K)$ , it may be concluded, because  $SO_2$  in combination with  $(SO_3K)$  must be more chlorous than  $SO_2$  in combination with (OK).

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and since the nitrosulphates can be thus written, they have no superior value to sulphates or thiosulphates in establishing that sulphur is sometimes sexualent. The reaction between these salts and the alkali metals, observed by Mr. Haga and myself,

$$K(N_2O_2)(SO_3K) + K_2 = K(N_2O_2)K + K(SO_3K),$$

shows that this view of their constitution is the proper one to take.

The Double Atom of Oxygen as a Radicle .- Nitrosulphates being no longer of value in determining the valency of sulphur, it becomes of greater interest than before to consider whether sexvalency or quadrivalency is shown by sulphur in sulphates. This point may be discussed in a very few words. If it is to be treated as anything more than a question of graphic representation, there cannot be much difficulty in deciding that sulphur behaves as a quadrivalent element in sulphates and all other sulphuryl compounds. For the same reasons which have led to the adoption of the view that sixteen, and not eight parts, by weight, of oxygen form in chemical change an indivisible part of a molecule of water or of a molecule of alcohol, must lead, if consistency is to be preserved, to the conclusion that the two atoms of oxygen in sulphuryl form a double atom, or single bivalent quantity, in the constitution of this and of some other chlorous radicles. Thus, there are no stages or breaks in the formation of compounds of sulphuryl as regards this radicle itself, and none in their decomposition, the sulphur taking up or losing its own weight of oxygen in one operation. In other words, sulphuryl compounds are not reducible to thionyl compounds, and thionyl compounds are not directly oxidisable to sulphuryl compounds, the special case of the conversion of the free oxides into each other being excepted. Thus, in ethanesulphonic chloride, or in a sulphone, reduced by a hydrogen mixture, the sulphuryl loses all its oxygen at once. Again, the radicle of sulphuryl hydroxychloride is either wholly removed, or not touched at all by hydrogen sulphide,  $8SO_2(OH)Cl + 5SH_2 = 6SO_2(OH)_2 +$  $6HCl + S_2Cl_2 + 5S$  (H. Prinz). The production of thionyl chloride from ethanesulphonic chloride and from benzenesulphonic chloride by phosphorus pentachloride has already been mentioned as being really a reaction between free sulphur dioxide and the pentachloride. But it is also stated in some books that Michaelis has found sulphuryl chloride to be slowly converted to thionyl chloride by phosphorus pentachloride. It must, however, be taken into consideration that this chemist has shown that phosphorus pentachloride decomposes sulphurvl oxychloride,  $S_2O_5Cl_2$ , into sulphur dioxide and chlorine : and

that sulphuryl chloride cannot be formed by means of phosphorus pentachloride, chlorine and sulphur dioxide (and not thionyl chloride) being produced instead. Any slow formation of thionyl chloride from sulphuryl chloride may, therefore, be attributed to a dissociation of the sulphuryl chloride into sulphur dioxide and chlorine in the first place, and then to the conversion of the dioxide into thionyl chloride by Schiff's well-established reaction.

An apparent exception to this statement of the non-oxidisability of thionyl to sulphuryl may occur to some in the case of ethylsulphine oxide, a thionyl compound capable of being oxidised to ethyl sulphone, a sulphuryl compound. As a fact, this oxide forms a well-defined nitrate, and this nitrate it is which, heated with nitric acid, yields the sulphone, thus:—

$$\mathrm{Et_2S} <_{\mathrm{OH}}^{\mathrm{ONO_2}} + \mathrm{HONO_2} = \mathrm{Et_2S} <_{\mathrm{O}}^{\mathrm{O}} + \mathrm{H_2O} + \mathrm{N_2O_4}.$$

Another apparent exception will be the conversion of sulphuric acid to sulphur dioxide by hot reducing agents. But here the sulphuric acid may be confidently assumed to first undergo dissociation into sulphur trioxide and water.

The Constitution of Sulphur Dioxide.—With regard to the conversion of sulphur dioxide to sulphur trioxide, I need merely point out that this occurs only under circumstances which serve as conditions for the development of active oxygen, and just those, therefore, which give us the double atom of oxygen, to be found in ozone,  $O \triangleleft O_2$ ,\* and hydrogen dioxide,  $H_2 \triangleleft O_2$ , substances produced also in such circumstances. It is to be noted of sulphur dioxide that it is in fact a body intermediate between sulphuryl and thionyl compounds, and may be considered either as  $S \triangleleft O_2$  or O:S:O as commonly treated. There is much to favour the view contained in the first of these formulæ. Thus, this being accepted, the union of sulphur dioxide with a base becomes similar to that of chlorine :—

$$Ca(OH)_{2} + SO_{2} = Ca \angle O \\ SO_{3} + OH_{2}.$$
$$Ca(OH)_{2} + Cl_{2} = Ca \angle O \\ Cl_{2} + OH_{2}.$$

Again, zinc ethide unites directly with sulphur dioxide to form

\* As a means of simplifying the writing of many formulæ, I think the symbol  $\triangleleft$  very convenient, and would therefore recommend its use. Thus, we may write  $O(NO)_2$ , but  $O\triangleleft(FeO)_2$  instead of  $O\begin{pmatrix}FeO\\|\\FeO\\FeO\end{pmatrix}$ ; and  $O(CH_3)_2$ , but  $O\triangleleft(CH_2)_2$  instead of  $O\begin{pmatrix}FeO\\|\\FeO\\FeO\end{pmatrix}$ ;  $CH_2$ 

ethane-sulphinate, and so, apparently, does zinc itself to form hyposulphite (Bernthsen), although in this case in the presence of water:---

$$\begin{aligned} \mathrm{Et}_{2}\mathrm{Zn} + 2\mathrm{SO}_{2} &= \frac{\mathrm{Et}}{\mathrm{Et}} \underset{\mathrm{SO}_{2}}{\overset{\mathrm{SO}_{2}}{\mathrm{Et}}} \, \cdot \\ \mathrm{Zn} + 2\mathrm{SO}_{2} &= \mathrm{Zn} \underset{\mathrm{SO}_{2}}{\overset{\mathrm{SO}_{2}}{\mathrm{H}}} \, \cdot \end{aligned}$$

Sulphur dioxide is reducible by zinc and acid to the simple hydride,  $-S \triangleleft$  to  $S: H_2$ —whilst the double atom of oxygen in sulphuryl compounds is not thus replaceable by hydrogen as it is in nitroxyl compounds, just for the reason that the atom of sulphur becomes fully saturated by two atoms of hydrogen, and cannot therefore take these when it is already in combination with other radicles. Where the attempt to force it to do so gives a result, as is usually the case,—for example, when ethanesulphonic chloride is treated with a hydrogen mixture,—the two atoms of oxygen are removed without being displaced by hydrogen, this element merely taking the place of the chlorine removed at the same time:—

$$\operatorname{EtS}_{\operatorname{O}_2}^{\operatorname{Cl}} + 6\mathrm{H} = \operatorname{EtSH} + 2\mathrm{OH}_2 + \mathrm{HCl}.$$

The reaction, however, which, for the present at least, must be regarded as establishing the formula O:S:O, is that of phosphorus pentachloride on sulphur dioxide—

$$O:S:O + Cl_2PCl_3 = Cl_2SO + OPCl_3$$
.

but it stands alone.

### Sulphites-their Place in a Series of Sulphuryl Compounds.

A brief review of sulphoxy-compounds considered as combinations of the radicles sulphuryl and thionyl may serve to strengthen the view that sulphites are not dioxylic. The conception of a compound radicle as a something in the composition of a molecule which is as much indivisible in many of the relations of the molecule as an atom, has apparently been much weakened by the doctrine of valency. Yet there is no sufficient reason for this. To see but little else in the property of phosphorus trichloride of combining with either two univalent chloride-atoms or one bivalent oxygen-atom than that phosphorus is quinquivalent, is to ignore the almost entire want of connection in properties between the pentachloride and oxychloride, and the fact that the latter is one of a series of compounds of a trivalent radicle phosphoryl as well defined as that of the compounds of a simple radicle. It would, indeed, be easy to show that it has been the failure to appreciate the connections of facts expressed by the theory of compound radicles which has done most to bring the theory of valency into disrepute.

Compounds	of Sulphuryl, $\equiv S \triangleleft O_2$ .
Sulphuric oxide, gaseous Sulphuric oxide, condensed.	$O: SO_2.$ $O_2S: O_2: SO_2.$
Thiosulphuric peroxide	$O_2S \triangleleft_{S=S}^{O O} \triangleright SO_2.$
Sulphuric peroxide, if $SO_4$ .	$O_2 \triangleright SO_2.$
[Sulphuric peroxide, if $S_2O_7$	$(?) O_2 S \underbrace{O}_{O} S O_2 \text{ or } O_2 S \underbrace{O}_{-O} S O_2].$
Sulphates	$(KO)_2SO_2; \begin{array}{c} EtO \\ KO \end{array} > SO_2; (EtO)_2SO_2.$
Thiosulphates	$     KO \\     KS > SO_2;     KO \\     EtS > SO_2. $
Nitrososulphates	$\mathrm{KO}_{\mathrm{K}(\mathrm{N}_{2}\mathrm{O}_{2})}>\mathrm{SO}_{2}.$
Pyrosulphites	${\rm KO}_{{\rm K(SO_2)}}>{\rm SO_2}$
Pyrosulphates	$\begin{array}{c} \mathrm{KO} \\ \mathrm{O} > \mathrm{SO}_2 \\ \mathrm{KO} > \mathrm{SO}_2 \end{array}$
Monothiopyrosulphates (tri-	$K_{\alpha} > S_{\alpha}$ $K_{\alpha} > S_{\alpha}$
Dithiopyrosulphates (tetra- thionates)	$\mathrm{KO}^{\mathrm{SSO}_2}; \mathrm{KO}^{\mathrm{SO}_2}; \mathrm{KO}^{\mathrm{SO}_2}$
Hyposulphates	KOSO₂ ↓ KOSO₂
Sulphites and sulphonates .	$\underset{KO}{\overset{KO}{\times}} SO_2;  \underset{Et}{\overset{KO}{\times}} SO_2;  \underset{Et}{\overset{EtO}{\times}} SO_2.$
Thiosulphites or thiosul- phonates	${}^{\mathrm{EtS}}_{\mathrm{Et}}$ >SO <sub>2</sub> .
Hyposulphites	$\begin{array}{ccc} \mathbf{KSO}_2 & \mathbf{EtSO}_2 \\   & ; & (?) &   \\ \mathbf{KSO}_2 & \mathbf{EtSO}_2 \end{array}$
Sulphinates and sulphones.	$\stackrel{\mathrm{Et}}{\mathrm{K}}>\mathrm{SO}_2;\qquad \mathrm{Et}_2\mathrm{SO}_2.$

Sulphuric Oxide Condensed.—The formula S<sub>2</sub>O<sub>6</sub>, adopted for this body by Michaelis, brings it into relation with the pentoxides of

nitrogen and phosphorus as bodies of the same type as their own salts :---

Nitroxyl nitrate	$(O_2N).O.NO_2$	like	KONO2
Sulphuryl sulphate	$(O_2S):O_2:SO_2$	,,	$\operatorname{BaO_2SO_2}$
Phosphoryl phosphate	(O P):O3:PO	,,	AlO <sub>3</sub> PO.

The reaction of sulphuric acid with mercury, copper, or silver, in which all the hydrogen of the acid is left as water, is to be treated as one occurring between the metal and sulphuryl sulphate,  $S_2O_6$ , into which and water sulphuric acid so readily dissociates, and is expressed by the equation—

 $(SO_2)SO_4 + Cu = CuSO_4 + SO_2.*$ 

Action of Sulphur Dioxide on Sulphites (this vol., p. 209).—To represent the reaction as occurring, in the first place, directly between the sulphuric acid and the metal, and then between *nascent* hydrogen and more of the acid, is a proceeding which will not bear criticism. It is opposed to the fact that metals of this class never do liberate hydrogen, and to the consideration that were hydrogen thus liberated it must, in order to be active, be assumed to have greater chemical power than the agent which set it free, and that, too, in order to enable it to recombine with oxygen immediately after having been separated from this very element.

Thiosulphuric Peroxide.---If the two common oxides of sulphur have

\* At a sufficiently low temperature, as shown by the thorough examination made by Pickering into the behaviour of copper with sulphuric acid, copper sulphide is formed. This formation I attribute to the decomposition of sulphur dioxide into oxygen and sulphur, which each combine with copper, thus :---

 $4\mathrm{Cu} + \mathrm{SO}_2 = \mathrm{Cu}_2\mathrm{S} + 2\mathrm{CuO},$ 

the CuO then becoming sulphate. At higher temperatures, the sulphide is also decomposed by the sulphuric acid. In support of this view, I may refer to the action of sulphur dioxide on stannous chloride or on phosphorous chloride, in both of which actions the dioxide is similarly decomposed, and its elements distributed among three molecules, thus :--

$$\begin{split} 3\mathrm{SnCl}_2 + \mathrm{SO}_2 &= \mathrm{SnCl}_2 + 2\mathrm{OSnCl}_2,\\ \mathrm{followed} \ \mathrm{by} \ 2\mathrm{OSnCl} + \ 4\mathrm{HCl} &= 2\mathrm{SnCl}_4 + 2\mathrm{H}_2\mathrm{O},\\ \mathrm{and} \ 2\mathrm{SSnCl}_2 &= \mathrm{S}_2\mathrm{Sn} + \mathrm{SnCl}_4,\\ \mathrm{or} \ \mathrm{SSnCl}_2 + \mathrm{SnCl}_2 &= \mathrm{SnCl}_4 + \mathrm{SnS}. \end{split}$$

In the case of phosphorous chloride :--

 $3PCl_3 + SO_2 = SPCl_3 + 2OPCl_3$ .

This reaction, however, occurs only at a red heat, but then that with thionyl chloride takes place at lower temperatures (Michaelis):--

 $3PCl_3 + Cl_2SO = Cl_2PCl_3 + SPCl_3 + OPCl_3$ 

See also a former paragraph.

the constitution represented by the formulæ O: S: O and  $O_2 \triangleright S: O$ , a peroxide may be looked for as able to exist, having the constitution  $O_2 \triangleright S \triangleright O_2$ . Unless Berthelot's peroxide contains this body, it is not yet known, but the compounds of sulphuric oxide with sulphur, selenium, and tellurium, examined by R. Weber, and by Shimosé and myself, appear to answer both in composition and properties to this peroxide with one atom of oxygen displaced by quadrivalent sulphur, selenium, or tellurium, and will, therefore, form a double molecule of the oxide, as shown by the formula in the table (see also Trans., 1884, 195).

Sulphuric Peroxide.—The formulæ I have suggested in the table for Berthelot's peroxide, if  $S_2O_7$ , are fanciful, but the only ones consistent with the view that sulphur is not more than quadrivalent. These formulæ are calculated to confirm the doubts which must be entertained of the existence of an oxide with such a composition. The formula for the peroxide as  $SO_4$  has been noticed in the previous paragraph, and leaves the sulphur quadrivalent.

Thiosulphates.—It is impossible to represent in a simple manner the formation of thiosulphates from sulphites, unless the latter salts are formulated as monoxylic.

The analogy of the decompositions of silver sulphite and silver thiosulphate by water, is worthy of notice here, as illustrating the uniform valency of sulphur in these salts and in sulphates :--

$$\begin{array}{l} {}^{\mathrm{AgO}}_{\mathrm{Ag}} > \mathrm{SO}_2 \, + \, \mathrm{H}_2\mathrm{O} \, = \, \mathrm{Ag}_2 \, + \, (\mathrm{HO})_2\mathrm{SO}_2. \\ \\ {}^{\mathrm{AgO}}_{\mathrm{AgS}} > \mathrm{SO}_2 \, + \, \mathrm{H}_2\mathrm{O} \, = \, \mathrm{Ag}_2\mathrm{S} \, + \, (\mathrm{HO})_2\mathrm{SO}_2. \end{array}$$

Böttger, like Berthelot, has found that other metallic oxides besides that of copper produce thiosulphates from alkali polysulphides. These reactions are all essentially forms, I consider, of that which takes place between sulphur and lime when heated with water, and which, in a recent paper, I have interpreted as being—(1) the formation of sulphur dioxide (sulphuryl) along with sulphide of the metal, (2) the union of the dioxide with base, and (3) the conversion of sulphite to thiosulphate. Thus, taking the case observed by Böttger, that of lead oxide (hydroxide) and sodium pentasulphide, I would express it somewhat like this :—

(1.) 
$$\operatorname{Na_2S_5} + 2\operatorname{PbO} = \operatorname{Na_2S_2} + 2\operatorname{PbS} + \operatorname{SO_2}$$
.  
(2.)  $\operatorname{SO_2} + \operatorname{PbO} = \operatorname{Pb} \bigtriangleup \operatorname{SO_2}$ .  
(3.)  $\operatorname{Pb} \swarrow \operatorname{SO_2} + \operatorname{Na_2S_2} = \frac{\operatorname{NaO}}{\operatorname{NaS}} \operatorname{SO_2} + \operatorname{PbS}$ .

Böttger sees in the effect of lead oxide on alkali tetra- and penta-

sulphides proof that these bodies are not the sulphur analogues of sulphites and sulphates. This effect, however, goes no farther than to show how much more readily reducible the polysulphides are than the sulphites and sulphates.

*Nitrososulphates.*—The constitution of these salts as sulphur compounds has already been noticed. As nitrogen compounds, their constitution will be further considered under nitrites.

Pyrosulphites or Sulphurylsulphates.—From Berthelot's experiments it seems very doubtful whether any true acid sulphites exist, that is, which are other than the pyrosulphites with water of crystallisation.

To represent pyrosulphites, as is done in the table, as having the group  $SO_2$  between half the metal and the sulphuryl, is in accordance with accepted views about anhydro-salts. Since sulphur dioxide in entering into combination behaves in all other cases as sulphuryl, it probably does so here, and therefore stands in the pyrosulphites with its sulphur joined to metal, thus:  $-\frac{O_2}{K-S-(SO_3K)}$ , making these salts to be intermediate between hyposulphates and hyposulphites:--

KOSO2	$KOSO_2$	$KSO_2$
ł		1
KOSO₂	$KSO_2$	KSO2

Accordingly, just as disulphuryl,  $S_2O_4$ , unites with a metal peroxide to form the first, and with a metal to form the last, so it unites with a metal monoxide to form a pyrosulphite (even in presence of water). Pyrosulphites may however be thionylsulphates:—KO—S—(SO<sub>3</sub>K), although most probably they are not.

The reality of this intermediate position is further shown by the facts that a pyrosulphite can be reduced by zinc or sodium to hyposulphite, and can be oxidised by lead dioxide, or by chloral, and other chloromethylic compounds to hyposulphate (Rathke).

Dithiopyrosulphates.—The double atom of sulphur in these salts, although hardly of noticeable occurrence in inorganic chemistry, is a well-marked and stable radicle in the organic bisulphides.

Hyposulphates.—Some chemists\* adopt for these salts a formula different from that here given to them, in which they appear as thionyl compounds, thus:— $(KO.SO)_2 \triangleleft O_2$ . But surely there is incongruity in the notion of peroxidised thionyl compounds, whilst there are no facts in the history of these salts which suggest such a view of their constitution.

Hyposulphates are also called dithionates, but this name, in so far as it indicates relationship to the other polythionic salts, is unsatis-

factory, whereas the older name of hyposulphates is perfectly appropriate in the set of names—sulphate and hyposulphate, sulphite and hyposulphite, as is shown by the formulæ for these salts given in the table. The other polythionic salts may be defined as those in which unoxidised sulphur unites two sulphuryl radicles, whilst hyposulphates are salts which contain no sulphur but that of sulphuryl. Hyposulphates oxidise directly to sulphates, in presence of acid, and reduce directly to sulphites in presence of base, and are strictly intermediate between these two classes of salts.

The formation of a hyposulphate by manganese dioxide is at once intelligible from the following equation :---



So is also its decomposition by sodium amalgam, when we use the monoxylic formula for a sulphite, as already shown on a previous page.

Berthelot finds that both copper oxide and zinc oxide convert alkali polysulphides not only into thiosulphate, but into hyposulphate and sulphate. The formation of the hyposulphate may probably be explained as due to the action of the sulphur of the polysulphide on alkali sulphite (which substance, according to what I have argued in a previous paper to the Society, is a transition-body in the formation of thiosulphate). This sulphur partly converts the sulphite into thiosulphate, but partly also into hyposulphate, thus :---

$$K_2S_2 + 2\frac{KO}{K} > SO_2 = 2K_2S + \frac{KOSO_2}{|KOSO_2|},$$

in accordance with Spring's reactions with iodine and with sulphur chloride, already noticed in this paper. The sulphate comes probably from the decomposition of zinc thiosulphate by zinc oxide, in accordance with the behaviour which some metallic thiosulphates show :—

$$\operatorname{Zn} \langle {}^{\mathrm{O}}_{\mathrm{S}} \rangle \mathrm{SO}_2 + \mathrm{ZnO} = \mathrm{ZnO}_2 \mathrm{SO}_2 + \mathrm{ZnS}.$$

For the passage of thiosulphate to hyposulphate observed by Ramsay, see below under "Hyposulphites."

Sulphites and Sulphonates.—A sulphonate should be defined as an organic sulphite. The sulphurous ethers at present called sulphites should cease to receive this designation, and might be called thionites.

Thiosulphites or Thiosulphonates.—Pauly and Otto have so clearly established the constitution of these bodies that the provisional term, disulphodioxides, might well disappear from text-books.

Hyposulphites.—Schützenberger makes his hydrosulphites to be salts of an acid  $H_2SO_2$ . His results have been called in question by Bernthsen, but even should they prove to be correct, the salts would still be sulphuryl compounds, corresponding with the sulphinates. Bernthsen, however, has adduced evidence which seems sufficient to justify chemists in accepting the formula  $H_2S_2O_4$  given by him to hyposulphurous acid, in place of  $H_2SO_2$ . I have written the hyposulphites in the table with a formula relating them to hyposulphates in the way of haloïd salts to oxylic salts, and placing them between sulphites and sulphinates just as the hyposulphates stand between sulphates and sulphites :—

 $\begin{array}{ccccccc} \text{KOSO}_2 & \text{KSO}_2 \\ \text{Hyposulphates} \dots & & | \\ \text{KOSO}_2 & & \text{KSO}_2 \\ \end{array} \\ \end{array}$ 

Such a constitution is a highly probable one; but without a fuller knowledge of these salts than we have at present, it cannot be regarded as established. Their mode of formation is expressed by the equation KSO<sub>2</sub>

already given :—Zn + 2SO<sub>2</sub> = Zn  $\triangleleft$  (SO<sub>2</sub>)<sub>2</sub>; also Zn + 2 | = KOSO<sub>2</sub>

 $(KSO_2)_2 + Zn(SO_3K)_2$ ; and the assumption that the zinc does not take oxygen is borne out by the fact that even zinc-ethyl does not do so in the act of forming its sulphinate with sulphur dioxide. Although hyposulphites might be written as compounds of oxide of metal with sesquioxide of sulphur, they have no relation in properties to the known sesquioxide, which is a peroxidised body.

$$2(SO_3K)SEt = (SO_3K)_2 + (SEt)_2;$$

and if we assume that ethylic thiosulphite behaves in like manner, thus :--

$$2(SO_2Et)SEt = (SO_2Et)_2 + (SEt)_{22}$$

forming hyposulphite, and that this reacts with potassium hydroxide. thus :---

$$(SO_2Et)_2 + OK_2 = (SO_2Et)OK + (SO_2Et)K,$$
  
R 2

we have Pauly and Otto's observed reaction :---

Thiosulphite. Sulphonate. Sulphinate. Bisulphide.  $2(SO_2Et)SEt + OK_2 = (SO_2Et)OK + (SO_2Et)K + (SEt)_2.$ 

Sulphinates and Sulphones.—The sulphinates are less stable than sulphones, because they are compounds of unoxidised metal. In their decomposition, no partial deoxidation occurs, but the separation of the sulphur and oxygen becomes complete in one molecule, these elements then converting other undecomposed molecules into thiosulphonate and sulphonate respectively.

One way of forming a sulphinate is to combine sulphur dioxide with an organo-zinc compound. This fact alone goes far to prove that sulphites are monoxylic; for if zinc ethide, a powerful reducing agent, in uniting with sulphur dioxide yields a compound of sulphuryl, that is, of sulphur that cannot be further oxidised, it seems certain that an oxygenous body, such as zinc hydroxide, will, in uniting with sulphur dioxide, not yield a compound of thionyl, that is, of sulphur capable of being further oxidised.

Compounds of Thionyl,  $\equiv S: O$ .

Thionyl oxide	0:80.
Thionyl chloride	$Cl_2SO.$
Ethyl thionite ("sulphite")	(EtO) <sub>2</sub> SO.
Ethyl potassium thionite	$_{\rm KO}^{\rm EtO}$ >SO.
Ethyl sulphine oxide	Et <sub>2</sub> SO.
(?) Thionamide	$(\mathrm{NH}_2)_2\mathrm{SO}_2$

Thinoyl oxide.—With the exception of the sulphine oxides, all thionyl compounds are readily convertible to sulphur dioxide. Thionyl chloride may be derived from sulphur tetrachloride, but it and all other thionyl compounds, except the sulphine oxides, are obtained directly or indirectly from thionyl oxide.

The formation of sulphites from sulphur dioxide, regarded as thionyl oxide, involves the occurrence of the change from that relation which exists between the sulphur and oxygen in thionyl to that which exists in sulphuryl. In whichever way sulphites are viewed, this change has to be met; but it is the practice at present to localise it, not here, but in the act of metallic sulphites passing into organic sulphites ("sulphonates"), or of these into metallic sulphites. In the conversion of thionyl oxide to a sulphite, it may be considered to be oxidised to sulphuryl by and then combined with a base, thus :---

 $SO_2 + 2KOH = OH_2 + KO(SO_2)K.$ 

Such an oxidation of a chlorous radicle by a base is no assumption; it is effected by potash acting on chlorine and some other simple bodies, and on benzaldehyde and other carbon compounds.

This explanation of the passage from thionyl to sulphuryl compounds is not one of the simplest, but it is much more satisfactory than any that can be devised of the interconversion of sulphites and sulphonates, on the usual supposition that the former are thionyl compounds. In the derivation of sulphites from other thionyl compounds, the intermediate production of thionyl oxide may, without doubt, be considered to take place.

Thionyl Chloride.-It seemed to me to be unnecessary to introduce the chloride and oxychlorides of sulphuryl into the list of compounds of that radicle, but thionyl chloride is of special importance amongst thionyl compounds, from its serving to fix the constitution not only of sulphur dioxide, but of the sulphurous ethers or "thionities."  $\mathbf{As}$ is well known, these ethers can also be formed from sulphur thiochloride or thio-thionyl chloride. Prinz has recently published his conclusion that this body,  $S_2Cl_2$ , has not the constitution of thionyl chloride, but I am unable to follow his argument. He has shown that Carius's reaction between phosphorus pentasulphide and (oxy) thionyl chloride does not yield the thio-thionyl chloride, as it is stated to do, but thionyl oxide, the chlorine, not the oxygen, going to the But there remains the work of Michaelis, of Thorpe, phosphorus. and of others: there is the very formation of the sulphurous ethers showing that the monochloride is the thiochloride of sulphur.

Prinz also records the results of several experiments made in the endeavour to replace the bivalent sulphur of the chloride by oxygen. These experiments were made by treating the thio-thionyl chloride with various oxides, and the result obtained was either negative, or else the oxides were converted to chlorides, and the sulphur chloride to sulphur and sulphur dioxide. But this was only to be expected, on any theory of its constitution, since sulphur will take oxygen in exchange for chlorine whenever the oxide of another element is present, which itself allows of such exchange. As Michaelis and Schifferdecker have shown, sulphur tetrachloride resembles phosphorous pentachloride in its property of exchanging chlorine for oxygen.

In saying, as Prinz does rightly enough, that thio-thionyl chloride behaves in some reactions like a mixture of sulphur with its tetrachloride, and in objecting for this reason to the view that it is the analogue of (oxy)thionyl chloride, he does not seem to have considered that this thionyl chloride itself—as he himself has pointed out—behaves sometimes as if it were a mixture of sulphur dioxide with sulphur tetrachloride :—

$$2SSCl_2 = S_2S + SCl_4.$$
  
$$2OSCl_2 = O_2S + SCl_4.$$

Ethyl Potassium Thionite.—This is Warlitz's salt with the constitution usually attributed to it, which appears to be the correct one. It stands apparently alone, and in this respect is of particular interest, as a metaloxyl compound of thionyl.

### Nitrites-no Evidence that they are Oxylic.

As in the case of sulphites, two views have been held concerning the constitution of nitrites, as expressed by the formulæ Ag.NO<sub>2</sub> and AgO.NO. The former was suggested by Odling to the Society, many years ago, as probably the correct one, but the latter is now held by him, and, perhaps, universally by chemists.

I feel compelled, as I have stated in a paper read before the Society in 1883, entitled "On the Production of Hydroxylamine from Nitric Acid" (Trans., 1883, 443), to go back to that view of the constitution of nitrites in which they are represented as haloïd or non-oxylic salts, and I now proceed to submit my argument, beginning, as in the case of sulphites, by endeavouring to show that there are no grounds to be found in the properties of nitrites for preferring an oxylic constitution for them. Such notions as the following have led to their being regarded as oxylic salts;--that all oxygenous salts are oxylic; that, because organic nitro-bodies are much more stable under certain conditions than metallic nitrites, they must be differently constituted; that the relations between nitrites and their organic derivatives appear simpler when nitrites are treated as oxylic than when they are treated as haloïd or non-oxylic; and that the element nitrogen cannot be in direct union with metallic elements in saline combinations, above all if these contain oxygen.

Combined nitrogen unites directly with metallic elements, even in the presence of water, and even in the presence of oxygen in the reacting compounds; and at high temperatures displaces oxygen already combined with metals.—Ammonia acts on some metallic oxides and hydroxides, and on some oxygen salts, to form compounds—and that, too, not only in the case of the silver-mercury class of metals—in consequence of the metal rejecting oxygen for nitrogen.

The metallic "cyanates" can exist in solution, and they contain both oxygen and nitrogen, and yet there are probably not two opinions as to their being carbosylamines,\* that is, so constituted as

<sup>\*</sup> I venture to call attention to the advantage of substituting, as I have done in the text, the word "carbosyl" for "carbosyl," not so much because its sound is softer, as that it admits of the syllable "thio-" being prefixed to it to form a name for the analogous sulphur radicle, which "carboxyl" of course does not: thus we

#### NON-SATURATED OXYGENOUS SALTS.

to have nitrogen, and not oxygen, joining the metal to the carbon, thus: O: C: N.Ag. To this fact may be appended the consideration that since there are two series of hydrocarbon derivatives of the radicle oxycyanogen and two of the radicle nitrogen dioxide, the one having the hydrocarbon joined to the nitrogen, and the other having it joined to the oxygen, and since the oxycyanogen compounds of the metals are like the more stable series, in which the hydrocarbon is not united to the oxygen, it ought surely to be the case that the more stable nitro-hydrocarbons, in which the carbon is again not united to the oxygen, are the analogues of the metallic nitrites.

In the metallic ureas, we find metal in combination with the nitrogen, instead of with the oxygen of the urea. The reaction of mercury oxide on a solution of thio-urea is strikingly in point as to the preference of some metals for nitrogen, although here we have to do with sulphur instead of oxygen :---

### $SC(NH_2)_2 + HgO = NCNH_2 + HgS + OH_2.$

The mercury, it is true, gets the sulphur, but not at once, for if it did, we should be left with urea, and that would certainly not become cyanamide. Instead of this, the mercury unites with the nitrogen and displaces the hydrogen, which with the oxygen of the metallic oxide forms the water, and then the mercury thio-urea breaks up into the simpler cyanamide and mercury sulphide.

Cyanamide forms salts, even in water, in which the metal is united with nitrogen. Also, when calcium carbamate\* is heated, calcium cyanamide, Ca: N.C: N, is formed by the calcium separating from the oxygen of the carbamate to unite with the nitrogen.

The simple metallic cyanides themselves appear much more like carbamines than like nitrils; they are poisonous, they oxidise to "cyanates" or carb s lamines, and they yield the organic carbamines in reactions in which the heat is not so great as necessarily to convert these into nitrils. Hydrogen cyanide, too, is related to the

get "thiocarbosylamine." [Dr. Divers appears to be under a misapprehension in terming the radicle CO carboxyl, a name which is invariably given to the radicle CO.OH; the radicle CO, as is well known, is always termed carbonyl by English writers, and there does not seem to be any want of a new name. H. E. A.]

\* Having mentioned this salt, I take the opportunity to claim some recognition of the part I had in its discovery. Drechsel now gets sole credit for this, but a reference to this Journal, 23, 230 and 361-363, will show that I, long before he had published his work, had pointed out the existence of this salt, and the effect of ammonia in preserving carbamates from decomposition, and had given a quantitative analysis of the calcium carbamate in combination with calcium chloride, a combination since examined by him, at least its analogue, the barium salt. In thus asking that my work may not be altogether ignored, I have no thought of denying to Drechsel the credit of his, so much more extended and exact than the incidental work of mine in this direction.

carbamines by its characteristic odour as well as by its poisonous quality; and since every carbamine yields formic acid when hydrolysed, the production of this acid from hydrogen cyanide does not make the latter a formyl compound, as usually represented, any more than it does any other carbamine. Cyanides being carbamines, why may we not, on the evidence of facts, write similar formulæ for two such similar salts as nitrite and cyanide of potassium?

Nitrite.... K.N:(O<sub>2</sub>)". Cyanide.... K.N:C".

The production of organo-nitroxy-compounds is in no case of a kind to favour the oxylic theory of the constitution of nitrites.—The mode of formation of the nitro-paraffins, by both Kolbe's and V. Meyer's methods, clearly favours the view that the nitrogen of nitrites is united with the metal, but the formation of the nitrolic acids may seem to be unfavourable to it. Yet this is not the case. Although, when the formation is formulated as usual, and after V. Meyer—

 ${\rm HO.NO} + {\rm H_2C} {<_{\rm NO_2}^{\rm Me}} {=} {\rm HON} {:} {\rm C} {<_{\rm NO_2}^{\rm Me}} + {\rm OH_2}.$ 

there seems to be a very simple cutting out of the oxygen and hydrogen to form water, and coming together of the bivalent organic residue and hydroximide, yet on consideration the appearance of simplicity will be seen to conceal intermediate changes which must occur. And when we do consider these, it will be found that the formula  $H.NO_2$  is more in accordance with accepted views of this mode of elimination of the elements of water, as I shall proceed to show.

A body with the constitution HONO should form water by exchanging NO for hydrogen, as, according to wide experience, hydrocarbon hydrogen takes hydroxyl in preference to non-hydrogenised oxygen. Here I may recall, as in point, what I drew attention to in my former paper, that Lössen's method of obtaining hydroxylamine from ethyl nitrate, shows that it is not the hydroxyl of nitric acid even, that on reduction becomes the hydroxyl of the hydroxylamine, since the hydroxyl of the nitric acid (ethoxyl of the ethyl nitrate) is the first to be removed by the reducing process. But to continue. With the formula  $H.NO_2$  the introduction of the hydroximide into the nitroethane is shown to proceed in the regular way; the oxygen atoms of the nitrite become hydroxyls; one of them along with the nitrite-hydrogen breaks off to form water; and the residual hydroximide and the nitroethane residue unite as required to form the nitrolic acid :---

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So, too, I think, with the formation of the nitrosamines, is it clear, that the non-oxylic constitution of the nitrites affords a satisfactory interpretation of the change, whilst the oxylic constitution does not, in spite of appearing to do so. Chemists now write—

 $Et_2NH + HO.NO = Et_2N.NO + OH_2$ 

and the matter looks simple enough. But if we would represent the substances that actually must be used in order for the desired reaction to proceed, we have to write—

 $H_2Et_2NCl + KONO = H_2Et_2N.O.N:O + KCl$ 

and then, only by some change of an "intramolecular" kind, that is, by a change which we do not see our way to represent rationally, can the diethylammonium nitrite become diethylnitrosamine and water. Now no such objection can be brought against the following equations, so far as I can see :—

> $H_2Et_2N.Cl + K.NO_2 = H_2Et_2N.NO_2 + KCl,$ and  $H_2Et_2N.NO_2 = Et_2N.NO + H_2O.$

The production of the diazoammonium or diazotammonium salts can be explained equally well by using either formula for the nitrite. With the new formula, the equation may be set out thus :---

$$\mathbf{N} \begin{cases} \mathbf{O} \\ \mathbf{O} \\ \mathbf{H} \\ \mathbf{H} \\ \mathbf{H} \end{cases} + \frac{\mathbf{H}}{\mathbf{H}} \\ \mathbf{N} \\ \mathbf{N} \\ \mathbf{N} \\ \mathbf{O}_{3} \\ \mathbf{N} \\$$

Metallic nitrites are oxidisable, and therefore unlike organo-nitroxybodies, because of the presence in them of unoxidised metal.—Potassium nitrite, like potassium sulphite, is oxidisable for the reason that potassium is oxidisable. The instability of silver nitrite is of a different kind; like silver sulphite, it is not simply oxidisable, and, again like the sulphite, it is unstable by first decomposing so as to yield metallic silver as one of the products. Nitroethane is not oxidisable, because ethyl is not so. Its decomposition when heated with water and hydrochloric acid, in which the ethyl is changed, is due, of course, to interaction of the nitroxyl with the ethyl.

# If Nitrites are not wholly Oxylic, then it is not true that all Oxygenous Salts are Oxylic.

Action of Phosphorus Oxychloride on Nitrites.—I have tried (again with the assistance of Mr. Shimidzu) the behaviour of silver nitrite

towards phosphorus oxychloride. There is considerable reaction, but in no case could we detect an oxychloride of nitrogen among the products. Nor did we succeed, even when we took more than twelve inolecules of nitrite to one of the phosphorus compound, in preventing some of the latter from distilling over unchanged, leaving behind unchanged nitrite through which it had passed for a thickness of several centimetres. In the residue were silver chloride and phosphate, with unchanged silver nitrite. Volatilised were phosphorus oxychloride unchanged, and the third oxide of nitrogen, this being condensable by a freezing mixture to a green liquid containing a very little phosphorus oxychloride. The absence of oxychlorides of nitrogen may perhaps be accounted for by the fact, observed by Exner, that nitroxyl chloride is decomposed by silver nitrite, as no doubt would also be nitrosyl chloride if formed.

As the crucial test for the presence of oxylic oxygen, therefore, the action of phosphorus oxychloride fails in this case, no oxychloride of nitrogen being obtained. The production of the third oxide of nitrogen is, indeed, quite in accordance with the view of the oxylic structure of nitrites, but it is in no way decisive. The decomposition of silver nitrite by a gentle heat into silver, silver nitrate, and different oxides of nitrogen, is, as I have already shown in a former paper, so ready,\* that, considering the imperfect action of phosphorus oxychloride on the silver nitrite, the results obtained are not remarkable on the view that the nitrites are non-oxylic salts. Indeed, it is difficult to see what simple reaction, with this constitution, could occur between the two compounds, or even how any reaction at all could happen were no traces of water or nitrate present in the nitrite. I believe pure and dry nitrites would be unaffected by pure phosphorus oxychloride.

The indication afforded by Exuer's reaction between nitroxyl chloride and silver nitrite, depends on the view taken of the constitution of the fourth oxide of nitrogen.

### Nitrites-Evidence that they have not an Oxylic Constitution.

The Quinine Test.—Silver nitrite at once destroys the fluorescence of a sulphuric acid solution of quinine. Other nitrites are less satisfactory, because of their entire decomposition by the acid.

Behaviour of the Silver Class of Metals and their Nitrites towards Nitric Acid.—The metals of the silver-mercury class never displace hydrogen from its combinations with oxygen. This fact comes out as clearly in the case of nitric acid as with any other hydroxyl-compound.

<sup>\*</sup> This Journal, 24, 85. In some preliminary experiments by Mr. Shimidzu and myself, silver nitrite in a vacuum gave off at a gentle heat the second oxide of nitrogen almost pure, probably by reaction between  $NO_2$  and  $AgNO_2$ .

This being so, in order to account for the production of silver nitrate from nitric acid and silver, I made (in a former paper already referred to) what appears to me still the only appropriate assumption, namely, that in the first place silver nitrite and silver hydroxide are formed as transition-bodies, thus:  $-2Ag + HONO_2 = HOAg + AgNO_2$ , these afterwards being converted to nitrate by more nitric acid. In doing this, however, I had overlooked the striking results obtained by Russell, and presented by him to the Society in a paper entitled "On the Action of Hydrogen on Silver Nitrate." Silver in dissolving in ordinary nitric acid actually does so as nitrite, but not also as hydroxide, for it dissolves only in nitric acid in the presence of a lower oxide or acid of nitrogen, a fact making the assumed formation of hydroxide unnecessary. I have to thank Dr. Armstrong for calling my attention to Russell's work, which I find of special value in connection with my present object. Indeed, this work gives practically all the facts I have to bring forward in direct support of the view that nitrites are non-oxylic salts.

We have in Russell's experiments proof, as nearly as possible, that silver, which cannot separate hydrogen from oxygen, separates it from nitrogen, and aided by this hydrogen then also dissolves in nitric acid itself, thus :  $-2Ag + HNO_2 + HONO_2 = 2AgNO_2 + H_2O$ . From this it would seem that nitrites must be non-oxylic, and thus different This explanation and equation, which I offered as a from nitrates. suggestion in my previous paper, to account for the much greater solvent power on silver of red nitric acid than that of the colourless acid, admits, however, of a modification, one which is greater in appearance than in reality. Nitrous acid has only a doubtful existence ever, and may not have one at all, even in presence of nitric acid. But then  $N_2O_4$  will be there, and that is the same as dehydrated nitric and nitrous acids together; then  $2Ag + (NO_2)_2 = 2AgNO_2$ , and silver is seen uniting directly with nitrogen, when unable to decompose the oxylic compound, nitric acid.

Russell's paper furnishes other evidence of the haloïd nature of nitrites. It is there pointed out that during the dissolution of silver in nitric acid, silver nitrite is formed in quantity, partly in solution in the silver nitrate liquor, partly as crystals. Its presence in solution is important, as showing that it is not the sparing solubility of the nitrite which causes its formation as insoluble matter. Now, if silver nitrite is an oxylic salt like the nitrate, this existence of silver nitrite in presence of nitric acid is as difficult to account for as its formation, for nitrites are ordinarily decomposable by the weakest acids. As a haloïd salt, the reason of its ability to exist in nitric acid is clear : silver tends to separate from oxygen, and combines much more stably with nitrogen than with oxygen.

I have tested this matter in another way, by treating silver nitrite with dilate nitric acid and with dilute sulphuric acid. The nitrite dissolves without either colour or effervescence, and from the solution alkalis precipitate it unchanged. When potassium or sodium nitrite is similarly treated, it effervesces like a carbonate and gives a coloured solution and gas, the reason for this difference being that potassium is unstably combined with nitrogen in presence of oxygen, or of an oxygen-compound—it is of the zinc-tin class of metals.

Again indebted to Russell, I have to point out that whilst silver nitrate in solution is converted by free hydrogen to silver and nitric acid, silver nitrite is wholly unaffected by this gas. There is no accounting for this fact, so long as both salts are regarded as oxylic, the true explanation no doubt being that hydrogen separates silver from oxygen, and cannot separate it from nitrogen.

Heat-decomposition of Ammonium Nitrate and Nitrite.—The decomposition of ammonium nitrate into water and nitrous oxide, and that of the nitrite into water and nitrogen, seem in marked agreement with the theory that the one salt is oxylic and the other not, as the following equations show :—

$$\begin{array}{ll} & O_2 \mathbf{N} \\ & \mathbf{H}_4 \mathbf{N} \\ \end{array} > O = 2O\mathbf{H}_2 + \begin{array}{||}{\mathbf{N}} \\ & \mathbf{N} \end{array} > O; \\ & & \mathbf{H}_4 \mathbf{N} \\ \end{array} = 2O\mathbf{H}_2 + \begin{array}{||}{\mathbf{N}} \\ & \mathbf{N} \\ & \mathbf{N} \end{array}$$

But I would remark that, for these decompositions to be regarded as positively favourable to the theory, they must be essentially different in nature from those which takes place when ammonium salts of other acids become amides. In these, dissociation into acid and ammonia must precede the formation of water and the amide\* by a reaction like the following, for example :—

# $(MeCO)OH + NH_3 = (MeCO)NH_2 + OH_2.$

It is probable enough, however, that the decomposition of the nitrate and nitrite is in reality different from that of most ammonium salts, in consequence of the readiness with which nitroxyl becomes deoxidised.

# Nitrites being Non-oxylic, there is no Evidence that Nitrogen is ever Quinquivalent towards Oxygen.

Nitrates and nitrites having the same radicle  $NO_2$ , there is not a single fact to support the notion that nitrogen is ever quinquivalent

\* Or, as I showed in 1870 in my paper "On the Combinations of Carbonic Anhydride with Ammonia and Water," free ammonia must be made to act on the ammonium salt. In this case, the ammonium being bound in oxylic combination with the acid radicle, the free ammonia attacks the oxygen of the ammonoxyl, forming amide and water, and thus setting free by its own destruction another molecule of ammonia to take its place. towards oxygen, as in nitrate compounds.\* Nitrogen is, indeed, quinquivalent in ammonium and oxyammonium (including sulphazo) salts, and therefore may be so in other compounds, but the nitrogen of or in ammonium salts is no more capable of oxidation by ordinary laboratory reagents than free nitrogen, and nothing but active oxygen or plant-life seems capable of oxidising it.

The Double Atom of Orygen as a Radicle.—The formation of nitrates in this way favours the notion of the nitrogen being united to a double atom of oxygen; and certainly the assumption that this is the case makes the chemistry of nitrate derivatives more easily intelligible. The non-existence of  $ON(OH)_3$ , and of  $ONCl_3$ , becomes a matter of course; so does the derivation of nitro-organic compounds, now from nitrate and now from nitrite, whilst the easy reducibility of these compounds to amides has already caused some chemists to write the radicle of nitrobenzene, for example :  $-N \triangleleft O_2$ , instead of  $-N \ll_O^O$ . That this double atom of oxygen is not so stable in nitroxyl compounds as it is in sulphuryl compounds seems due to the much weaker combination existing between nitrogen and oxygen than between sulphur and oxygen.

The quinquivalency of phosphorus to oxygen being so well established, and the periodic relations of the elements so certain, it is of moment to point out in connection with the tervalency of nitrogen to oxygen here deduced, that in the odd series the members of Group V are distinguished by an alternate rise and fall in degree of stable valency. Thus, nitrogen and arsenic pentachlorides are unknown, whilst those of phosphorus and antimony exist; nitric acid and arsenic acid readily yield oxygen, whilst phosphoric acid and antimonic acid are much more difficult to deoxidise. This alternation is not confined to Group V, but extends to the whole series, chlorine and iodine forming higher oxides than fluorine and bromine, sulphur and tellurium higher than oxygen and selenium.

Nitroxyl and Nitrosyl Compounds.—The radicle  $--NO_2$  being the same whether it comes from nitrites or from nitrates, organo-nitrobodies are evidently true organic nitrites, whilst the nitrous ethers are not, but in reality oxylic compounds of nitrosyl. As such they might be well called *nitrosites*. The only sources of these ethers are compounds of nitrosyl, principally the third oxide of nitrogen. Of

<sup>\*</sup> It is stated in my paper on Hydroxylamine, that the chemical equation used therein to express the reduction of nitrate to nitrite is of interest "in representing the nitrogen as undergoing no change in quantivalence." My meaning has been somewhat misunderstood, and I see that I ought to have written, "in not representing the nitrogen as undergoing any change in quantivalence;" for it is in this respect that it differs from the equations usually given.

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the existence of free nitrous acid there is simply nothing known. The formation of nitrous ether simultaneously with the true nitrites or nitroethane by the reaction between ethyl iodide and silver nitrite, may be considered as due to a secondary effect produced by the heat of the first change. The nitroethane is thus transformed to nitrous ether by the occurrence of a first step in that change which so readily proceeds, in which the nitroethane becomes acetic acid and hydroxylamine (V. Meyer), thus :---

(1.) Dry nitroethane...  $C_2H_5NO_2 = C_2H_5.ONO.$ 

(2.) With water and acid  $C_2H_5$ .ONO +  $OH_2 = C_2H_4O_2 + H_2NOH$ .

The relative stability of nitroethane and nitrous ether depends, of course, on circumstances; under the condition of raised temperature, the nitrous ether is the more stable; in the presence of water, the nitroethane is the more so.

Too little is definitely understood concerning the constitution of the oxides of nitrogen to allow of the actual passage of nitrosyl compounds to nitroxyl compounds being profitably discussed at present. It will therefore suffice to point out that the formation of a metallie nitrite from the third oxide of nitrogen and a base, differs from the formation of an ethylic nitrosite from the same oxide and an alcohol, in being a case of oxidation of an acid radicle similar to the action of a base on chlorine or other acid radicle, and indeed on sulphur dioxide as sulphuryl.

Hyponitrites and Sulphuric Hyponitrites.—In connection with the theory here maintained, as to the non-oxylic character of unsaturated oxygenous salts, something must be said of hyponitrites and the nitrous radicle of sulphuric hyponitrites or nitrososulphates. That hyponitrites are non-oxylic I believe to be certain, but at present I am not prepared to say more. Zorn has proved that hyponitrites are bibasic, and that ethyl hyponitrite is not what I call an oxylic ether, although he writes this ether (somewhat inconsistently)

## Et.O.N: N.O.Et.

Had it this oxylic structure it would readily decompose with potassium hydroxide, and this, according to him, it does not do, even in presence of alcohol. Hyponitrites can be written as non-oxylic by giving them -N-O

a radicle, | |, or preferably,  $\equiv N - N \triangleleft O_2$ , having in either case -N - O

the double atom of oxygen, thus :---

$$Ag_2N.N \triangleleft O_2 \text{ and } \frac{K}{(SO_3K)} > N.N \triangleleft O_2.$$

These formulæ are here given only as possibilities.

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### The Lower Acid Oxides are not true Anhydrides.

Sulphur dioxide and nitrogen trioxide are the anhydrides of the thionylic and nitrosic ethers, but they are not the anhydrides of sulphites and nitrites, if this term is used strictly. In uniting with basic oxides, they function like chlorine, as acid radicles. In confirmation of the truth of this conception of their nature, the recent researches of Reinitzer (*Ber.*, 14, 1886) may be mentioned. This chemist has shown that phosphorus trioxide does not appear to be the anhydride of the phosphites.