LV.—*Mercury Sulphites, and the Constitution of Sulphites.*

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Introduction.

THE compounds described in this paper are, in formation and constitution, not ordinary salts, since they can scarcely be prepared by the ordinary process of double decomposition—that of bringing in contact a sulphite with a mercury salt having the mercury in a relation corresponding to what it is to have in the mercury sulphite. The study of these compounds should form a not unimportant part of the chapter in chemistry relating to the constitution of salts; for they are compounds of the non-saturated oxygenous radicle, SO_3, with one of that group of metals—silver, mercury, and copper—the members of which are distinguished by their inability to displace hydrogen, the relative stability of their compounds with nitrogen, sulphur, and the halogens, and their property of forming more than one series of salts in which they are strongly basic.* As such, these salts serve admirably to supply facts for the determination of the particular constitution of non-saturated oxygenous compounds.

Nothing in the properties of the sulphites of the metals had ever, we believe, been regarded as evidence that they are not dioxylic salts until notice was called to the matter by one of us in a paper read to the Society last year. When, long ago, the organic sulphites were found to be hemioxylic only, there seemed to be differences enough between them and mineral sulphites to separate them from the latter, and consequently they were made into a class called *sulphonates*, whilst the mineral sulphites were left with the dioxylic constitution attributed to them, of which some of their properties were supposed to indicate the possession. It soon became apparent, however, that this separation of the organic from the inorganic sulphites was not based upon any radical difference of constitution, for sulphite and sulphonate passed smoothly one into the other in reactions of double decomposition. The effect of recognising this has not been a happy one, as, instead of establishing anything, it appears to have unsettled the views entertained concerning the constitution of oxygenous salts, and nourished a belief that there is little that can be

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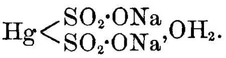
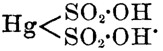
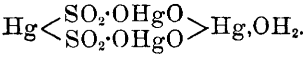
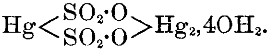
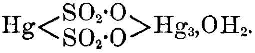
* The intimate relationship of these metals, as thus defined, with the adjacent iron-platinum metals is obvious. To differentiate them from this group would hardly be in place here.

definitely said about it. Davy's theory, that oxygenous salts are binary compounds of a metallic radicle with a compound haloïd radicle, having been overthrown in the course of the development of the chemistry of carbon compounds, there has been an evident unwillingness to admit the force of facts which seem to require that this theory in a modified form should be in part reinstated. Witness in proof of this statement the efforts made to minimise the difference in basic character between the third atom of hydrogen in phosphorous acid and the other two. There can hardly be said to be any evidence, however, against certain oxygenous acids (those which are oxidisable to other acids) being partly or wholly compound haloïd acids; and all that would seem to be wanted is more evidence from inorganic sources than has as yet been brought forward in order to gain for non-saturated oxygenous acids a less reserved admission that they have a partly haloïd or non-oxylic constitution. The admission is one which seems to us pregnant with consequences, such as we indicate in another section of this paper; for it is in effect that an acid may have two kinds of basic hydrogen in consequence of constitution or structure.

Origin of Mercury Sulphites.—When it might be supposed that mercuric sulphite would be formed by direct double decomposition, it does one of three things, according to circumstances; it forms with another basylous radicle a double sulphite such as mercuric sodium sulphite or mercuric hydrogen sulphite; it forms a basic or oxysulphite with oxide of mercury taken from the nitrate or other mercuric salt; or it forms mercuroso-mercuric sulphite by suffering partial hydrolysis into sulphuric acid and its mercury element. Again, when mercurous sulphite would be expected there appears, instead, a salt metameric with it, hypomercuroso-mercuric sulphite. It is in this manner that the following mercury sulphites are formed in place of mercuric and mercurous sulphites, both unknown:—

Mercuric sodium sulphite	 $\mathrm{Hg}<\begin{matrix}\mathrm{SO_2{\cdot}ONa}\\ \mathrm{SO_2{\cdot}ONa}\end{matrix},\mathrm{OH_2}.$
Mercuric hydrogen sulphite ?*..	 $\mathrm{Hg}<\begin{matrix}\mathrm{SO_2{\cdot}OH}\\ \mathrm{SO_2{\cdot}OH}\end{matrix}.$
Mercuric oxysulphite	 $\mathrm{Hg}<\begin{matrix}\mathrm{SO_2{\cdot}OHgO}\\ \mathrm{SO_2{\cdot}OHgO}\end{matrix}>\mathrm{Hg},\mathrm{OH_2}.$
Mercuric mercurous or mercurosic sulphite	 $\mathrm{Hg}<\begin{matrix}\mathrm{SO_2{\cdot}O}\\ \mathrm{SO_2{\cdot}O}\end{matrix}>\mathrm{Hg_2},4\mathrm{OH_2}.$
Mercuric hypomercurous or hypomercurosic sulphite	 $\mathrm{Hg}<\begin{matrix}\mathrm{SO_2{\cdot}O}\\ \mathrm{SO_2{\cdot}O}\end{matrix}>\mathrm{Hg_3},\mathrm{OH_2}.$

History of the Mercury Sulphites.—Mercury sulphites have already been examined by Rammelsberg, Péan de Saint-Gilles, Hirzel, Wicke,

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* Known only in solution.

and A. Vogel. St.-Gilles has done most on the subject. Of the sulphites described in this paper, only mercuric sodium sulphite and mercuric oxysulphite have been previously described—both by St.-Gilles. The other sulphites of mercury described by these chemists we make out as having no existence, namely, St.-Gilles' normal mercuric sulphite, Wicke's mercurosic hydrogen sulphite, St.-Gilles' dimercuric sodium sulphite, and Rammelsberg's mercurous anhydrosulphite.

Normal Mercuric Sulphite unknown in the Separate State.

According to St.-Gilles, *normal mercuric sulphite*, $Hg''SO_3$, separates as a white, curdy precipitate, exceedingly unstable, obtained, but not in the pure state, when a syrupy solution of mercuric nitrate, free from excess of nitric acid, is treated with a dilute solution of normal sodium sulphite; either this salt, or *mercuric oxysulphite*, $(OHg_2''SO_3)_2$, or a mixture of the two, may be obtained in this way according as the mercury nitrate employed happens to be more or less basic. But, assuredly, St.-Gilles is wrong.

Mercuric Nitrate and Sodium Sulphite.—When normal mercuric nitrate, in presence of that very small amount of nitric acid which seems to be essential to its existence even in concentrated solution, is treated with a solution of normal sodium sulphite, *mercuric oxysulphite* is, from the first, precipitated in a pure or nearly pure condition, and, as a consequence, the mother-liquor proves to be much more acid than the original nitrate solution. The accumulation of this free acid soon prevents the precipitation of more oxysulphite, while much mercuric nitrate yet remains in solution. The addition of more sodium sulphite is now followed by momentary effervescence of sulphur dioxide, and a partial blackening of the white precipitate. This blackening effect was observed by St.-Gilles, and he has given, as conditions of successful preparation of the sulphite and of the oxysulphite, avoidance of excess of the precipitant and the employment of the nitrate solution in the concentrated state and the sulphite solution in the dilute state.

But when, as above described, some blackening has taken place, it soon disappears on agitating the precipitate with the mother-liquor, and, indeed, the mother-liquor may now be used to furnish more precipitate which, black at first, soon becomes white, provided too much sodium sulphite is not added. This white precipitate, however, consists not of the oxysulphite, but of another salt, *mercurosic sulphite*. Now this salt contains mercury in the proportion of only $1\frac{1}{2}$ atoms instead of 2 to 1 atom of sulphur, and its admixture with the oxysulphite in some of St.-Gilles' preparations may be the reason of his having found that the composition of the precipitate sometimes approached that of the normal sulphite. There is another circumstance of which St.-Gilles was unaware, and which must have affected his results: the oxysulphite contains water, and is efflorescent.

The production of a basic precipitate and an acid mother-liquor by adding normal sodium sulphite to normal mercuric nitrate, settles the matter so far as concerns the supposed production of normal mercuric sulphite in this way; and a word or two on St.-Gilles' view as to the conditions which determine the composition of the precipitate is better given here than when describing the preparation of the oxysulphite. He referred the degree of basic composition of the precipitate to the degree of basic composition of the solution of nitrate used. This view of the matter depends on the supposition that nitric acid will dissolve oxide of mercury in excess of the quantity required to form the normal nitrate. It is known, however, that this property is not possessed by nitric acid; when nitric acid, sp. gr. 1·4, is treated with a paste of precipitated mercuric oxide and water, dissolution can only be carried to a certain extent before a flocculent precipitate (which is white in total absence of chloride) of basic nitrate begins to separate, and the filtered solution contains normal nitrate with a minute quantity of free acid. It is in fact impossible by any method to get a basic nitrate solution. St.-Gilles, therefore, must have got the oxysulphite just as we have done, from normal nitrate, and not, as he supposed he did, from a basic or oxynitrate.

The fact that the formation of the oxysulphite is accompanied by that of free acid is also evidence as to the non-existence of mercuric sulphite. The oxysulphite is indeed insoluble in very dilute nitric acid, and if dissolved in stronger acid it rapidly undergoes a change to mercurous sulphate. (See further the section "Mercuric Oxysulphite," p. 546.)

The substitution of a solution of *mercuric sulphate* for the nitrate is, we may assume, attended with a similar result. Mercuric oxysulphite is not, indeed, precipitated, nor perhaps could it be, because of its solubility in sulphuric acid not exceedingly dilute; this acid being necessarily present as the means of keeping the mercuric sulphate in solution. But the mixed solutions, at first clear, soon begin to deposit mercurous sulphate, which is just what happens with a solution of mercuric oxysulphite in dilute sulphuric acid. The substitution of *silver sulphite* for sodium sulphite makes no difference; the insoluble silver sulphite becomes replaced by the insoluble mercuric oxysulphite, and silver nitrate forms in the solution, together with free acid. (See "Mercuric Oxysulphite," p. 551.)

Sodium sulphite and *mercuric chloride* also fail to give mercuric sulphite, the double sulphite of mercury and sodium being formed in this case

Mercurosic Sulphite and *Mercuric Chloride.*—By adding mercurosic sulphite to excess of solution of mercuric chloride, there is obtained, besides mercurous chloride, what appears to be a solution of normal mercuric sulphite in mercuric chloride, if not rather one of chloride-sulphite, $Hg(SO_2OHgCl)_2$.* The solution becomes acid also, but this is accounted for by the continual decomposition of the sulphite which goes on, whereby it becomes sulphuric acid and mercurosic sulphite again; this with the mercuric chloride yields more mercurous chloride and soluble sulphite, and so on. This is the nearest approach to a solution of the normal sulphite we know of. The reaction by which it is produced is—

$$Hg(SO_2O)_2Hg_2 + HgCl_2 = Hg(SO_2O)_2Hg + (HgCl)_2,$$

while its decomposition by hydrolysis is expressed by—

$$3Hg(SO_2O)_2Hg + 2OH_2 = 2SO_4H_2 + 2Hg(SO_2O)_2Hg_2.$$

Hypomercurosic sulphite behaves like mercurosic sulphite towards mercuric chloride.

Silver Sulphite and *Mercuric Chloride.*—Silver sulphite is decomposed by mercuric chloride, yielding ultimately silver chloride, mercurous chloride, and sulphuric acid:—

$$Ag_2SO_3 + OH_2 + 2HgCl_2 = 2AgCl + (HgCl)_2 + SO_4H_2.$$

A change of the mercuric chloride is thus effected in the cold which can only be accomplished by free sulphurous acid in hot solution. The primary action of silver sulphite, however, is to form mercuric sulphite or chloride-sulphite, which then suffers hydrolysis into sulphuric acid and mercurosic sulphite, from which point the decomposition proceeds as described in the section on "Mercurosic Sulphite." By pouring excess of mercuric chloride solution on to silver sulphite and quickly filtering, a solution is obtained which continues to deposit mercurous chloride for some time. The primary reaction is therefore—

$$2Ag_2SO_3 + 3HgCl_2 = 4AgCl + Hg(SO_2OHgCl)_2.$$

Sulphurous Acid and *Mercuric Oxide.*—Precipitated mercuric oxide can be dissolved in excess of an aqueous solution of sulphur dioxide, and can also under suitable conditions form with it an insoluble compound, mercurosic sulphite, but not normal mercuric sulphite. St.-Gilles states that when mercuric oxide in water is treated with sulphur dioxide, and the white substance produced is very quickly filtered off,

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* Mercuric chloride certainly does help to keep *mercuric hydrogen sulphite* in solution (see "Mercuric Chloride and Sulphurous Acid," p. 557, in section on Mercuric Hydrogen Sulphite Solution.)

the filtrate almost immediately deposits a white precipitate which is a mixture of normal mercuric sulphite with mercurous sulphate. The precipitate obtained in this way, however, is simply mercurosic sulphite, like the white substance first produced, and is only liable to be mixed with a little mercurous sulphate when the filtrate from which it has deposited has been allowed to stand for a much longer time than that indicated by St.-Gilles.

Mercuric sodium sulphite, when treated with a little *dilute nitric acid* or sulphuric acid, yields an insoluble sulphite of mercury; this, however, is mercurosic sulphite. (See the next section.)

The only conclusion possible therefore is that mercuric sulphite has no stability, except in combination with other sulphites, or with mercuric oxide or chloride.

Mercuric Sodium Sulphite.

Our purpose has not been to include in the investigation which is the subject of this paper the double sulphites of mercury with other metals, but it would have been impossible to gain a comprehensive notion of the relations of the single sulphites, without studying the properties of at least one of the alkali double sulphites, especially as normal mercuric sulphite is unknown. Double sulphites of mercury are readily obtainable, and several of them are known. They are all mercuric salts, while the double sulphites of copper are equally all cuprous.

Mercuric sodium sulphite has already been described by St.-Gilles. Besides the ordinary sulphite, which is half of sodium and half of mercury, he has described another which is two-thirds a sulphite of mercury. The former is the subject of this section of our paper; the latter is noticed in the short section following.

Properties.—Mercuric sodium sulphite is a comparatively stable salt, colourless, crystalline, very sparingly soluble in water and neutral to litmus (St.-Gilles*). It contains water, and its composition, as ascertained by St.-Gilles, is expressed by the formula $Hg(SO_3Na)_2,OH_2$. It requires about 25 parts of cold water to dissolve it. It may be preserved for a time but little changed. It slowly turns grey, however, and decomposes into mercury, sodium sulphate, and sulphur dioxide. Heated moderately, in the dry state, it evolves much sulphur dioxide together with the water it contains; at the same time it turns brownish and greyish. When the residue is

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* We write this section, like the rest of the paper, all from our own experience, except when we state otherwise, but whenever our observations are not the first recorded, we add a reference to the previous observer.

wetted, it blackens, through the formation of a flocculent, brownish-black matter, in small quantity, the principal products being metallic mercury and sodium sulphate. The brown-black matter heated with water changes into a pure black substance, insoluble in hot dilute nitric acid, and apparently sulphide. The main change effected by dry heat is probably the same as that by hot water, but a little mercuric sodium thiosulphate would seem to be also produced, by a reaction between the sulphur dioxide and some as yet undecomposed mercuric sodium sulphite. (Comp. Divers, Trans., 1885, 208.)

Heated in aqueous solution, it is converted into mercury, sulphur dioxide, and sodium sulphate :—

$$Hg(SO_3Na)_2 = Hg + SO_2 + SO_4Na_2.$$

The change is a sudden one (St.-Gilles).

According to St.-Gilles, mercurous sulphate is one of the first products of the decomposition of mercuric sodium sulphite by hot water, but blackens rapidly and then dissolves, leaving only metallic mercury. These are his equations modernised :—

$$\begin{aligned}2Hg(SO_3Na)_2 &= Hg_2SO_4 + Na_2SO_3 + Na_2S_2O_5\\ &= 2Hg + 2Na_2SO_4 + 2SO_2.\end{aligned}$$

We have not observed the formation of mercurous sulphate, and do not consider it possible that it could be formed. When the mercury comes out, it has a peculiar, we might say characteristic, appearance, familiar probably to many chemists; it appears as a bright rolling cloud, suggesting a precipitate of great volume, an effect due apparently to metallic reflection of light; this cloud then melts away, leaving a relatively minute, very dark grey deposit of mercury at the bottom of the vessel, the bright *mist* becomes, so to speak, a *rain* of mercury. These phenomena must have deceived St.-Gilles. Mercurous sulphate would not come out of solution from an abundance of hot acid liquid, and it cannot exist in presence of sodium sulphite, to the action of which it is exceedingly sensitive, and, therefore, would hardly be produced along with it. A single mercury sulphite when heated with water (mercuric oxide or other mercury compound being absent), becomes mercury and sulphuric acid; in the double sulphite, the sulphuric acid produced acts on the sodium sulphite, giving sodium sulphate and sulphurous acid.

The effect mentioned below of sodium hydroxide, sodium sulphite, or sodium chloride, in preventing decomposition of mercuric sodium sulphite in a hot solution, seems to show beyond doubt that the decomposition which occurs in absence of all such substances depends on the presence of acid, developed in minute quantity by the incipient decomposition of the salt. As to the sodium chloride, that will be effective through its displacing the sulphuric acid from the sulphite by hydrochloric acid, which is incapable of causing any liberation of mercury from the double sulphite. Since acid is the cause of the change, the formation of mercurosic sulphite will precede that of free mercury. (See below.)

Sodium hydroxide is without action when in dilute solution (St.-Gilles); in its presence a solution of mercuric sodium sulphite can be boiled without decomposing. If, however, the sodium hydroxide is added in somewhat large quantity and in concentrated solution, it precipitates some of the mercuric oxide, slowly in the cold, rapidly in the hot solution. Some only of the oxide is precipitated, and this is the scarlet-red form, instead of the usual orange-yellow one. In thus yielding the *red* oxide, mercuric sodium sulphite resembles black mercuric oxychloride. *Potassium hydroxide* precipitates mercuric potassium sulphite, which is much less soluble than the sodium salt. Mercuric oxide is not precipitated from the potassium salt by the most concentrated solution of potassium hydroxide, even when hot.

Hydrochloric acid changes it into mercuric sodium chloride and sulphurous acid. *Nitric acid* (or *sulphuric acid*) sufficiently diluted, and not in great excess, yields mercurosic sulphite, sodium sulphate and nitrate, and sulphur dioxide, thus—

$$3Hg(SO_3Na)_2 + 4HNO_3 = 4NaNO_3 + Na_2SO_4 + Hg_3(SO_3)_2 + 3SO_2 + 2OH_2.$$

In this complex change, the mercuric sulphite will not be decomposed by the nitric acid itself, for dilute nitric acid does not decompose mercury sulphites. The double salt will first exchange its sodium for the hydrogen of the nitric acid, and then the mercuric hydrogen sulphite will suffer partial hydrolysis and be converted into mercurosic sulphite, sulphuric acid, and sulphurous acid, in the way described in the section on "Mercuric Hydrogen Sulphite Solution" (p. 556). The addition of a little acid to a solution of mercuric sodium sulphite makes it smell of sulphur dioxide, but does not cause immediate precipitation. Some greyish mercurosic sulphite may soon precipitate, but in any case mercury is gradually set free. The acidified solution behaves, in fact, as one of mercuric hydrogen sulphite (which see for particulars). *Sulphurous acid* is without apparent action.

Sodium sulphite, in dilute solution, is without action, but its presence stops the decomposition of mercuric sodium sulphite by heat; in concentrated solution, it precipitates much of the mercuric sodium sulphite, which is much less soluble in it than in water, slightly soluble only as it is in the latter. *Sodium chloride* solution is without action; it prevents (St.-Gilles), or almost prevents, the usual decomposition when mercuric sodium sulphite is heated alone with water. The evaporated solution deposits crystals of the mercuric sodium sulphite unchanged, according to St.-Gilles. Sodium hydroxide has no effect on the boiling mixed solutions, indicating that there is no mercuric chloride present in the mixture. *Potassium iodide* is without action (St.-Gilles), when the sulphite is in solution. Solution of the iodide added to the solid sulphite gives a little crimson (not yellow or scarlet) precipitate, not further examined. The mother-liquor, or a mixed solution of the sulphite and iodide, gives a precipitate of ordinary mercuric iodide, when treated with sulphur dioxide (see p. 544).

Mercuric chloride solution, in the cold, is without action; but when the solutions are hot, mercurous chloride, sodium sulphate, and sulphur dioxide are produced :—

$$Cl_2Hg + Hg(SO_3Na)_2 = (ClHg)_2 + SO_4Na_2 + SO_2.$$

Or, as St.-Gilles found, hydrochloric acid may be formed (and then there will also be sulphuric acid)—

$$2OH_2 + 3Cl_2Hg + Hg(SO_3Na)_2 = 2HCl + 2(ClHg)_2 + SO_4Na_2 + SO_4H_2.$$

This occurs only when the mercuric chloride is in excess, the two acids then resulting from the well-known reaction between mercuric chloride and sulphurous acid. (St.-Gilles represents the change differently.) It is almost certain that the formation of mercurous chloride is due to the independent decomposition of the mercuric sodium sulphite, for when this is prevented by the addition of sodium chloride no change of mercuric chloride to mercurous chloride takes place. Mercurosic sulphite is formed from the mercuric sodium sulphite by the action of traces of sulphuric acid, and the mercuric chloride then acts on it, as described in the section on "Mercurosic Sulphite," to yield mercurous chloride and sulphuric acid again; so that once started, the decomposition of the sulphite proceeds very quickly. *Mercuric iodide* is without action in the cold. Heated, it is converted into the yellow iodide, and ultimately to mercurous iodide apparently. The reaction will be similar to that between the sulphite and mercuric chloride.

Mercuric oxide (precipitated) is without action in the cold, but warmed with the solution it gradually gives place to somewhat grey mercurosic sulphite, sodium sulphate being also formed. Most probably some decomposition of the mercuric sodium sulphite first occurs, as usual, into sodium sulphate, mercurosic sulphite (or mercury), and sulphurous acid, and then the sulphurous acid reacts with the mercuric oxide to form more mercurosic sulphite and sulphuric acid, which with sodium sulphite gives sodium sulphate and sulphurous acid, and so on.

Mercuric nitrate solution (aqueous nitric acid saturated with precipitated mercuric oxide), in excess, dissolves mercuric sodium sulphite, and then very rapidly yields a precipitate of mercuric oxysulphite. Provided the mercuric nitrate solution is somewhat concentrated (10 per cent. or stronger), and free from avoidable excess of acid, oxysulphite alone is precipitated if the mercuric sodium sulphite is added at once in quantity small enough to leave much of the nitrate undecomposed, and consequently not to generate too much nitric acid in this solution. The formation of the oxysulphite appears to be the only reaction of the mercuric nitrate itself, but other changes occur, owing to the nitric acid set at liberty:—

$$3Hg(NO_3)_2 + Hg(SO_3Na)_2 + 2OH_2 = 2NaNO_3 + 4HNO_3 + (OHg_2SO_3)_2.^*$$

The mother-liquor of the oxysulphite, treated with more mercuric sodium sulphite, yields at first mercurosic sulphite, and then gradually mercurous sulphate. When the quantity of the sulphite first added to the mercuric nitrate is too great, mercurosic sulphite may or may not be precipitated, but the oxysulphite which is formed remains in solution, soon, however, to pass, with marked rise of temperature, into mercurous sulphate, which then crystallises out. In this case, it is sometimes quite practicable to pour the mother-liquor off from the mercurosic sulphite, before the mercurous sulphate begins to separate. Mercurosic sulphite can always be obtained by adding the mercuric nitrate gradually to the mercuric sodium sulphite. It is no doubt formed, in either case, through the action of the nitric acid present on the mercuric sodium sulphite, and of liberated sulphurous acid on the mercuric nitrate; whilst the mercurous sulphate is the result of a metameric change of the mercuric oxysulphite in solution in the nitric acid.

Mercurous nitrate solution precipitates mercurosic sulphite:—

$$Hg(SO_3Na)_2 + (HgNO_3)_2 = 2NaNO_3 + Hg(SO_3)_2Hg_2.$$

Mercurosic sulphite prepared in this way is always of a light buff colour, although when formed by hydrolysis it is brilliantly white. When the nitrate solution is free from nitrous acid, and, so far as possible, from nitric acid also, only traces of sulphuric acid are formed. Nitric acid, in precipitating mercurosic sulphite, generates sulphuric acid, as already explained.

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[*] In the section on "Mercuric Oxysulphite," the nature of this remarkable reaction, and others related to it, is discussed under the heading "*Formation.*"

Mercuric sulphate solution does not precipitate mercuric oxysulphite, in consequence, apparently, of the solubility of the latter in sulphuric acid. The mixed solution soon deposits mercurous sulphate. By adding quickly about an equivalent quantity of the mercuric sodium sulphite, mercurosic sulphite can be precipitated. By adding a little *strongly* alkaline solution of mercuric sodium sulphite to excess of concentrated mercuric sulphate solution, mercuric oxysulphite can be precipitated. The mercuric sulphate solution used to prove this fact was made by saturating rather concentrated aqueous sulphuric acid with precipitated mercuric oxide, and contained only a very small quantity of free sulphuric acid.

Mercurous sulphate behaves like the nitrate, when it is shaken in the solid state with solution of mercuric sodium sulphite. It is then quickly changed to mercurosic sulphite.

Formation and Preparation.—Mercuric sodium sulphite is formed in reactions between—

(*a.*) A solution of *sodium sulphite*, or *sodium pyrosulphite* ("acid sulphite") and any *mercury sulphite.*

(*b.*) A solution of *silver sodium sulphite* and *mercuric oxysulphite.*

(*c.*) A solution of *sodium hydroxide* and any *mercury sulphite.*

(*d.*) A solution of *sodium chloride* and any *mercury sulphite.*

(*e.*) A solution of *sodium sulphite* or *pyrosulphite* and an *oxide*, or a *haloïd salt*, or an *oxylic salt*, whether *mercuric* or *mercurous.* Mercury cyanide is, however, an exception, being here inactive, although it reacts with ammonium sulphite, according to St.-Gilles. Yellow and green mercury iodides are also inactive among haloïd salts.

Concerning *a*, *b*, *c*, and *d*, consult the accounts of the several sulphites.

e. Sodium sulphite in dissolving mercuric oxide sets free sodium hydroxide. Sodium pyrosulphite and mercuric oxide yield no byeproduct. Hirzel first employed mercuric oxide and a pyrosulphite for preparing mercuric ammonium sulphite. Sodium pyrosulphite and mercuric oxide afford an excellent means of preparing the double sulphite in quantity. As much heat is evolved in the reaction, it is necessary to cool, especially if the solution of sodium pyrosulphite is concentrated; if allowed to get hot, the mercuric sulphite becomes hydrolysed, yielding mercury and sulphuric acid. If excess of mercury oxide has been added, it can be dissolved by adding a little more sodium pyrosulphite. The crystalline precipitate of double sulphite can be washed with a little water and well drained. Should it contain any mercury, through the solution having been allowed to get hot, the salt can be dissolved in hot water, to which a little sodium hydroxide has been added, and the solution filtered and set aside to crystallise, or precipitated with alcohol. When sodium sulphite is used in place of the pyrosulphite, the double sulphite is not decomposed if the solution becomes hot, and may therefore be at once drained, and then washed with alcohol, in order to remove sodium hydroxide.

Mercuric chloride is a very convenient source of the double sulphite; concentrated solution of the sulphite or pyrosulphite being poured on to the finely-powdered chloride. As it is exceedingly soluble in these solutions, no precipitation of double sulphite occurs until the sodium salt has been added in sufficient quantity. At first the salts formed are the two double salts (St.-Gilles) :—

$$2HgCl_2 + 2Na_2SO_3 = Hg(Cl_2Na)_2 + Hg(SO_3Na)_2,$$

but the further addition of sodium sulphite converts the double chloride to sodium chloride only, and brings down most of the mercury as double sulphite. If the mixture is heated when the mercury chloride is in excess, decomposition ensues (*see* "Mercuric chloride and mercuric sodium sulphite," p. 541). Sodium sulphite at once dissolves mercuric iodide as it does the chloride, but pyrosulphite has no action on it, strange to say, whilst sulphurous acid even precipitates mercuric iodide from its solution in sodium sulphite.* Mercurous chloride and mercurous oxide behave like the mercuric compounds, but half the mercury remains in the free state, the other half forming the double mercuric sulphite.

St.-Gilles found that mercuric oxide, chloride, and iodide, and mercurous chloride yielded the double sulphite. But, besides these haloïd salts, oxylic mercury salts, nitrates, and sulphates, both mercuric and mercurous, also furnish this compound; they should be added, mercuric salts especially, to the sodium salt gradually and not in excess, because in excess they destroy the double salt in the manner already described. This decomposition led St.-Gilles to believe that only haloïd salts could be used for making the double sulphites. In the case of the mercurous salts, half the mercury becomes free necessarily, but even with mercuric salts, a very little mercury, at least, is also set free; it is possible to get even half the mercury of the mercuric salt free, if the sulphite is not added in sufficient quantity for some time. The first effect of adding sodium sulphite to mercuric nitrate, for example, is to form mercuric oxysulphite and nitric acid :—

$$4Hg(NO_3)_2 + 2Na_2SO_3 + 2OH_2 = 4NaNO_3 + 4HNO_3 + (OHg_2SO_3)_2,$$

---

* Sulphurous acid also precipitates mercuric iodide from a solution of mercuric sodium sulphite to which potassium iodide has been added not in excess. It does not decompose mercuric sodium iodide.

and this oxysulphite dissolved in the nitric acid, or even lying in it, gradually changes to mercurous sulphate; on now adding more sodium sulphite, this mercurous sulphate yields ultimately only half its mercury as double sulphite, and half in the metallic state. By using the sodium sulphite at once in some excess, this is avoided, and almost all the mercury is converted into the double salt. The nitrates and sulphates, however, cannot be recommended for the preparation of the double salt, the oxide and chloride are far more advantageous. The formation of mercuric sodium sulphite from mercurous salts—nitrate, sulphate, chloride—is preceded by that of hypomercurosic sulphite, which is then resolved by more sodium sulphite into mercuric sodium sulphite and metallic mercury (see "Hypomercurosic Sulphite").

Chemical Composition.—We have not considered it necessary to confirm St.-Gilles' analysis of mercuric sodium sulphite; but something may be here said as to the constitution ascribed to it in this paper. If instead of $Hg<\begin{matrix}SO_2ONa\\SO_2ONa\end{matrix}$ mercuric sodium sulphite had the formula $Hg<\begin{matrix}OSO_2Na\\SO_2ONa\end{matrix}$, that is, had its mercuric radicle been half oxylic, or if it had the formula $Hg<\begin{matrix}OSO_2Na\\OSO_2Na\end{matrix}$, in which the mercury is represented as wholly oxylic, the cause of the relative stability of the double salts, of the non-existence of simple mercuric sulphite, and of many of the special reactions of the double salts, would cease to be apparent. There would also be no explanation why mercuric sodium sulphite has no action on litmus, and is not oxidisable by the air, whilst sodium sulphite is strongly alkaline and very oxidisable. With the constitution expressed by the formulæ $Hg(SO_2ONa)_2$ and $Na(SO_2ONa)$, sodium sulphite is alkaline, because of the instability of the non-oxylic union of sodium with sulphuryl, in presence of water, whilst in the mercuric sodium sulphite there is, through the absence of sodium so situated, the same indifference to litmus as is shown by sodium sulphate. Sodium sulphite is oxidisable, and mercuric sodium sulphite is not, because the non-oxylic sodium is oxidisable, and mercury is not; $Na(SO_3Na)$ oxidises to $NaO(SO_3Na)$, but $Hg(SO_3Na)_2$ undergoes no such change.

St.-Gilles' Dimercuric Sodium Sulphite believed not to Exist.

St.-Gilles obtains the mercuric sodium sulphite just described by adding mercuric chloride to excess of sodium sulphite, and then evaporating to crystallisation; but, as pointed out in the preceding section, by using solid mercuric chloride in powder, in place of its very dilute cold solution, the double sulphite can be obtained, without evaporation, as a precipitate.

Besides this double sulphite, he gets another, formulated as $Hg_2Na_2(SO_3)_3,OH_2$, by employing hot saturated solutions, the mercuric chloride being in excess; some mercurous chloride is formed, which he directs should be filtered off, and the filtrate left to cool. We have, however, failed to confirm his statements. With solutions hot enough, a most abundant formation of calomel occurs, and on cooling nothing separates, except sometimes crystals of the excess of mercuric chloride. With solutions less hot, the precipitation of calomel is slow and imperfect, so that the warm filtrate continues to deposit calomel in crystals, but no new double sulphite.

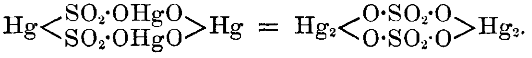
St.-Gilles asserts that the solution of this double salt has an alkaline reaction. It is difficult to see why this should be so. The filtrate from the calomel which should yield this salt is markedly *acid*, as a necessary consequence of the precipitation of calomel having occurred in it. Indeed, St.-Gilles himself mentions in another place this formation of acid along with calomel (see the action of mercuric chloride on the double sulphite in preceding section, p. 541). For our own part, we can hardly conceive of any way in which such a sulphite could be formed, considering that mercuric sulphite in the separate state is unknown.

Mercuric Oxysulphite.

Mercuric oxysulphite was first obtained in 1852, by St.-Gilles, and is the only one out of the three sulphites of mercury, which have been described, the existence of which we admit.

Properties.—Mercuric oxysulphite is a curdy, or granular, dense salt, insoluble in water, and very unstable (St.-Gilles). It has a faint yellow colour, and its composition is expressed by the formula $(OHg_2SO_3)_2OH_2$. Left to itself in the air at common temperatures, it changes, in some hours, into mercurous sulphate; but in a vacuum over sulphuric acid, it can be preserved for days partly undecomposed. It is thus rendered anhydrous, but in this state consists largely of mercurous sulphate: St.-Gilles represents the salt as anhydrous when precipitated. As pointed out by him, mercuric oxysulphite (in its anhydrous state) is metameric with mercurous sulphate. In ordinary moist air, it appears to change completely into this salt, but when heated even very gradually the change is not so simple:—

Mercuric oxysulphite. Mercurous sulphate.



$$Hg{<}\begin{matrix}SO_2{\cdot}OHgO\\SO_2{\cdot}OHgO\end{matrix}{>}Hg = Hg_2{<}\begin{matrix}O{\cdot}SO_2{\cdot}O\\O{\cdot}SO_2{\cdot}O\end{matrix}{>}Hg_2.$$

Mercuric Oxysulphite is Explosive.—This salt is remarkable in being exceedingly, though not violently, explosive. The explosion is attended by a moist, mercurial fume, the scattering of powdery particles, and by a dull sound when in a confined space. A temperature of 73° is sufficient to cause its explosion, but any quantity of it can at once be exploded at common temperatures, by touching the least portion of the whole with a heated body. It can also be exploded on the anvil, although its decomposition is so gentle that any noise produced is lost in that of the blow of the hammer. According to St.-Gilles, it is simply transformed into mercurous sulphate when heated; this salt is, indeed, the main product, but mercury and mercuric sulphate are also produced in quantity, besides water, of course, and a trace of mercuric oxysulphate. Only when slowly effected by warmth and moisture, is the change into mercurous sulphate perfect, or nearly so. It seems best to regard the decomposition of mercuric oxysulphite as being primarily, like that of the other mercury sulphites, one of hydrolysis. The first product will then be mercury, sulphuric acid, and mercuric oxide:—

$$(OHg_2SO_3)_2 + 2OH_2 = 2OHg + 2Hg + 2SO_4H_2.$$

The acid will then react with the mercuric oxide to form mercuric sulphate, and this in its turn with a portion of the mercury to form mercurous sulphate. The hydrolysis of the other sulphites of mercury to metal and acid, and of mercuric sulphate to oxide and acid, gives every probability of the correctness of the assumption here made respecting that of mercuric oxysulphite. As for the secondary union of mercury with mercuric sulphate, that can be readily effected in the cold, experimentally, in the presence of water containing very little sulphuric acid. But the mercuric oxide will also, when hot, act as an oxidising agent upon undecomposed oxysulphite, and thus determine the explosion. In proof of this, we have ascertained that a mildly explosive mixture can be made from precipitated mercuric oxide and either of the other mercury sulphites.

Water causes mercuric oxysulphite to decompose more rapidly than it does when kept dry. Heated with water it decomposes, the change being at first probably the same as when it is heated dry; but the water effects a further change, and the products are mercurous sulphate, mercuric oxysulphate, sulphuric acid, and mercury. When dissolved in aqueous solution of sulphurous acid and boiled, it decomposes in the manner which seems normal to a non-basic mercury sulphite, the sole products being mercury and sulphuric acid.

Potassium hydroxide converts it into mercuric oxide insoluble, and mercuric potassium sulphite in solution:—

$$Hg(SO_2OHgO)_2Hg + 2KOH = Hg(SO_2OK)_2 + 3HgO + H_2O.$$

Hydrochloric acid, added in excess at once, converts it into mercuric chloride and sulphurous acid. Hydrochloric acid, gradually added, causes the change of part of it into mercurosic and even hypomercurosic sulphite, by the sulphurous acid liberated from another part; more hydrochloric acid then forms mercurous chloride. If it has changed at all into mercurous sulphate, some mercurous chloride and sulphuric acid will also be produced, but sulphurous acid, even in the nascent state, has no action on mercuric chloride in the cold. If, again, it contains any of its mother-liquor of mercuric nitrate, reactions will take place on adding the hydrochloric acid, which will also produce mercurous chloride and sulphuric acid, the liberated sulphurous acid forming mercurosic sulphite from the nitrate, and the mercurosic sulphite forming mercurous chloride with the mercuric chloride. (See "Mercurosic Sulphite," p. 563.)

Nitric acid, or even *sulphuric acid*, if sufficiently dilute, hardly dissolves it, but hastens its change to mercurous sulphate. When a little more concentrated, the nitric or sulphuric acid dissolves it, *without liberating sulphur dioxide*, and then, if hydrochloric acid is added to the solution without delay, mercuric chloride and sulphur dioxide are formed in considerable quantities, besides some mercurous chloride and sulphurous acid.* But if the solution is kept for a few minutes, mercurous sulphate takes the place of the mercuric oxysulphite, and soon begins to separate. The addition of hydrochloric acid now produces only mercurous chloride and sulphuric acid. Sufficiently strong sulphuric or nitric acid liberates sulphur dioxide at once from mercuric oxysulphite.

Sulphurous acid, free or nearly free from sulphuric acid, when added in excess at once, dissolves it without forming any sulphate or sulphuric acid, and leaving mere traces of metallic mercury, the result of previous change in the oxysulphite; when, however, the sulphurous acid is added gradually, mercurosic sulphite is formed, then hypomercurosic sulphite, and, lastly, metallic mercury, as the quantity of sulphurous acid increases, while the solution from the first contains sulphuric acid, and, for a time, a little (acid) mercuric sulphite. The precipitation of mercurosic sulphite is also quickly induced when the sulphurous acid is added at once, provided it contains a good quantity of sulphuric acid. The later changes, here described, are treated of in subsequent sections of this paper; the formation of the mercurosic sulphite is represented by the equation—

$$3(OHg_2SO_3)_2 + 6SO_3H_2 = 4SO_4H_2 + 4Hg_3(SO_3)_2 + 2OH_2.$$

The effect of boiling the solution of mercuric oxysulphite in sulphurous acid has already been stated.

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* Sulphuric acid can, of course, only be detected as formed, when it has not been used.

Sodium sulphite solution, added quickly in excess, dissolves it as mercuric sodium sulphite; a minute quantity of metallic mercury is left, due to the presence of a little mercurous sulphate formed by previous change of the oxysulphite. Sodium hydroxide is also formed:—

$$(OHg_2SO_3)_2 + 6Na(SO_3Na) + 2OH_2 = 4OHNa + 4Hg(SO_3Na)_2.$$

When the sodium sulphite is added gradually, however, black, flocculent hypomercurosic sulphite is first seen, which is subsequently resolved into mercury and mercuric sodium sulphite. This production of hypomercurosic sulphite seems to prove that when only partially attacked by sodium sulphite, the mercuric oxysulphite is decomposed in such a way that the basic oxide is removed, and the normal sulphite left to suffer a change practically the same as hydrolysis, but effected by the sodium hydroxide which has been formed along with it, instead of by water. Thus:—

$$2Hg(SO_2O)_2Hg_3O_2 + 8Na(SO_3Na) + 4OH_2 = 2Hg(SO_2O)Hg + 4Hg(SO_3Na)_2 + 8NaOH.$$

$$2Hg(SO_2O)_2Hg + 4NaOH = Hg(SO_2O)_2Hg_3 + 2Na_2SO_4 + 2OH_2.$$

Silver sodium sulphite solution dissolves mercuric oxysulphite, all the silver being precipitated, principally as sulphite. The precipitate is much discoloured, apparently by the presence of a little mercuric argentous sulphite (coming from mercurous sulphate). Silver oxide scarcely appears, because the original solution always contains some free sodium sulphite, and accordingly sodium hydroxide is found in solution instead.

Sodium chloride solution forms mercuric oxide, yellow and insoluble, and mercuric sodium sulphite and mercuric sodium chloride, both in solution:—

$$(OHg_2SO_3)_2 + 4NaCl = 2OHg + Hg(SO_3Na)_2 + HgCl_4Na_2.$$

A little mercurous chloride is found with the oxide, and a little sodium sulphate in the solution, owing to the mercuric oxysulphite having begun to change into mercurous sulphate by the time it is prepared for experiment.

Potassium iodide solution changes mercuric oxysulphite instantly into a dull red compound, soluble in excess of the reagent, but with much more difficulty than simple mercuric iodide, and then yielding an alkaline solution. This dull red substance is of complex nature, and consists of mercuric iodide, oxide, and sulphite, in some state of combination. Except when the solution of potassium iodide is very concentrated, the dissolution of the red compound is at once followed by the appearance of a slight yellow precipitate convertible by a stronger solution of potassium iodide into a minute quantity of metallic mercury and dissolved mercuric iodide. The production of this yellow iodide is to be referred to the presence of some mercurous sulphate in the mercuric oxysulphite.

Mercuric chloride solution acts slowly on mercuric oxysulphite, if at all, mercurous chloride being gradually produced, together with mercuric sulphate which remains in solution with the excess of mercuric chloride. By dissolving mercuric oxysulphite in sulphuric acid before adding the mercuric chloride, the precipitation of mercurous chloride begins immediately, and proceeds rapidly until all the sulphite has been decomposed. Mercuric chloride has probably no action on mercuric oxysulphite, its action being on the mercurous sulphate into which the oxysulphite so readily changes. The action of mercuric chloride on other mercury sulphites is sharp and unmistakable, and in their case the completion of the action is retarded, instead of advanced by the presence of sulphuric acid.

Mercuric iodide, *oxide*, *nitrate*, and *sulphate*, and also *mercurous nitrate* and *sulphate* are without action. *Silver nitrate* also is without action on the oxysulphite itself, but a little silver is taken up apparently through reaction with the mercurous sulphate present.

Formation and Preparation.—Mercuric oxysulphite is formed in reactions between—

(*a.*) Solutions of *sodium sulphite* or *mercuric sodium sulphite* and *mercuric nitrate;* or solutions of *sodium sulphite* or *mercuric sodium sulphite*, *strongly alkaline*, and of *mercuric sulphate*.

(*b.*) *Silver sulphite* and *solution of mercuric nitrate*.

a. It was prepared first from sodium sulphite and mercuric nitrate by St.-Gilles, who states that other mercuric salts cannot be employed. In this statement he is practically correct, but by adding a strong solution of potassium or sodium hydroxide to the solution of sodium sulphite, this solution can be made to precipitate the oxysulphite from mercuric sulphate and yet leave an acid mother-liquor.

Held in acid solution, the mercuric oxysulphite soon becomes mercurous sulphate. If, without using alkali, the attempt is made to neutralise sulphuric acid by adding more sodium sulphite, mercurosic sulphite is precipitated. Mercuric oxysulphate cannot be used, as from its insolubility sodium sulphite would, for a time, be in excess in the solution.

Mercuric Nitrate and Sodium Sulphite.—Consult the account already given of the reactions between these substances, and between mercuric nitrate and mercuric sodium sulphite. The mercuric nitrate solution should not be too dilute; St.-Gilles used even a "syrupy" solution. Such concentration is unnecessary, but there should be at least one of nitrate in ten of solution. The sodium sulphite solution is better when rather dilute; a 5 per cent. solution answers well. Both solutions should be free from chloride, otherwise mercurous chloride will be found with the oxysulphite. The sodium sulphite should be in quantity small enough to leave much mercuric nitrate undecomposed, and be added to the nitrate all at once, and with stirring. A larger yield of oxysulphite may be obtained by mixing sodium hydroxide with the sodium sulphite, but the oxysulphite is then less easily purified. The use of mercuric sodium sulphite in place of sodium sulphite is an improvement, because although it causes the liberation of as much nitric acid as the single sulphite, it generates only half as much sodium nitrate for the same quantity of oxysulphite.

Mercuric oxysulphite cannot be washed much without being rendered impure by decomposition into mercurous sulphate, and the mercuric nitrate cannot be all washed out of it by water alone, because this precipitates basic nitrate; a little nitric acid must be added to the water. Another difficulty in the way of washing the precipitate is that it is far less stable in the moist state, when mercuric nitrate is absent. The process of purifying the oxysulphite without washing by spreading it in a thin layer upon a good porous tile, has proved very satisfactory, the mother-liquor being withdrawn from it very thoroughly, and it is left as a dry, undecomposed powder, when scraped from the tile after 20 or 30 minutes (but this process is not satisfactory when, by using free alkali, mercury nitrate has been too far replaced by sodium or potassium nitrate). When well prepared, the oxysulphite should be of a pale-yellow colour, dissolve in hydrochloric acid to an almost clear solution, and be very explosive. In precipitating, it is for a moment curdy, and then becomes granular.

b. The decomposition of mercuric nitrate by silver sulphite is a very interesting fact, which depends largely, no doubt, on the relative instability of oxylic mercury salts, such as the nitrate, in comparison with the oxylic silver salt, but would seem from other evidence to be partly due also to a firmer union of sulphuryl directly with mercury than with silver: in the reaction, the silver takes the place of sodium. The silver sulphite is added to excess of the mercuric nitrate with trituration, when it is quickly replaced by mercuric oxysulphite as the insoluble matter. As is the case when sodium sulphite is used, only a part of the mercuric nitrate can be precipitated as oxysulphite; more than sufficient silver sulphite for this purpose, no doubt, produces more oxysulphite, but this now remains dissolved in the nitric acid which has been formed, and soon becomes mercurous sulphate, which crystallises out. Prepared from silver sulphite, mercuric oxysulphite is more distinctly yellow, and always retains a very little silver,* which washing with mercuric nitrate solution does not remove. No useful quantitative analysis therefore could be made. It is highly explosive, slowly changes to mercurous sulphate, loses water on exposure, and in all respects is identical with that otherwise prepared.

Chemical Composition.—Mercuric oxysulphite is readily distinguished. Hydrochloric acid shows it to be a sulphite. Sodium hydroxide and sodium chloride both precipitate yellow mercuric oxide from it, and thus show it to be a mercuric salt and a basic compound. Hydrochloric acid also shows it not to be a mercurous salt, and, therefore, not one of the other sulphites of mercury. Its entire volatility, when previously moistened and then heated to nearly a red heat, shows the absence of alkali salt. Its great explosibility when dry is not only quite characteristic, but may be made a test of its freedom from alkali salt, which even in very small quantity greatly lessens this quality. Its gradual conversion into mercurous sulphate is evidence of its ultimate composition, and the simultaneous decrease in weight, proof of its containing water. The fume arising from its explosion also is damp. Some conversion to mercurous sulphate cannot be avoided during its preparation for analysis, but not necessarily to a greater extent than to cause its hydrochloric acid solution to be somewhat opalescent, and contain an insignificant amount of sulphate. Mercuric oxysulphite differs much in appearance from the other mercury sulphites; it is of a pale-yellow colour and forms a dense precipitate, at first curdy, then granular; hypomercurosic sulphite on the contrary is black and flocculent, whilst mercurosic sulphite forms a vividly white, voluminous, sometimes crystalline, precipitate.

By attributing to the oxysulphite a constitution in which one-fourth of its mercury is entirely in non-oxylic union with the sulphuryl, its reactions are made most capable of receiving consistent representation as well as its property of resisting the action of nitric acid (see the section on the general constitution of mercury sulphites). Although most mercuric oxysalts have three times the proportion of mercury proper to the normal salt, the oxysulphite has only twice, because it is only half an oxylic salt, and, as such, has only half as much extra base as the wholly oxylic basic salts. This is shown by

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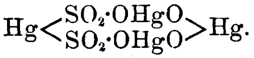
* Apparently as silver sulphate. Prepared from sodium sulphite, the oxysulphite takes up a very little silver when shaken with silver nitrate solution, and retains it during washing. Mercurous sulphate and silver nitrate do, we find, yield silver sulphate and mercurous nitrate.

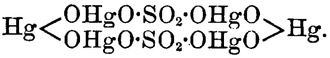
comparing the formulæ of the sulphite with that of the oxysulphate ("yellow turpeth mineral"):—

Oxysulphite.



$$Hg<\begin{matrix}SO_2\cdot OHgO\\ SO_2\cdot OHgO\end{matrix}>Hg.$$

Oxysulphate.



$$Hg<\begin{matrix}OHgO\cdot SO_2\cdot OHgO\\ OHgO\cdot SO_2\cdot OHgO\end{matrix}>Hg.$$

The results of St.-Gilles's analyses of the oxysulphite were not concordant, and led him to believe that it was mixed with more or less normal sulphite. We analysed our preparations by dissolving them in hydrochloric acid containing a little bromine, and then exposing the solution to air, without heating, until it became colourless. The sulphuric acid was precipitated first as barium salt; and then the mercury as sulphide, which was finally dried at 105—110°. Water was estimated from the loss, first in an air-pump desiccator, and then in an oven not heated above 60°. Exposure in the desiccator for 50 hours removed nearly all the water; the further exposure of 20 hours giving only an additional milligram loss. The salt now contained much sulphate, but was still explosive. Exposure to a heat of 55—60° for six hours destroyed the explosiveness of the salt, and caused a further loss of a milligram (salt taken = 0·656 gram). This loss may have been water, or it may have been mercury; we took it as the former. Heated now for six hours at 120°, it lost 2 mgrms.; this loss we regarded as mercury, and testing the residue found a little mercuric sulphate in it:—$OHg_2SO_3 = Hg + HgSO_4$. Analyses I and II were made considerably earlier than III and IV, and in very hot weather; the preparations were also exposed for a longer time on the tile. Preparations III and IV were sensibly dry, and formed non-coherent powders. Loss of water by efflorescence and by conversion to mercurous sulphate all tells on the mercury percentage number, because mercury constitutes four-fifths of the salt. III was washed with water slightly acidified with nitric acid; the others were not washed. All four were different preparations. A portion of the salt prepared for analysis IV was ignited to see to what extent it might be impure from retained bye-products; the residue amounted to 0·17 per cent.:—

	I.	II.	III.	IV*a*.	IV*b*.	$O_2Hg_4(SO_3)_2OH_2$.
Mercury ..	79·64	79·81	78·71	78·60	—	79·21
Sulphur ..	6·50	6·35	6·66	6·60	—	6·34
Oxygen ...	—	—	—	—	—	12·67
Water	—	—	—	—	1·86	1·78
						100·00

Mercuric Hydrogen Sulphite unknown in the Separate State.

Haloïd salts of mercury always give a mercuric alkali sulphite when treated with an alkali sulphite; but Wicke states that by treating solid mercuric chloride with a solution of sodium pyrosulphite he prepared mercuric hydrogen sulphite. He is certainly wrong. A solution of sodium pyrosulphite readily dissolves mercuric chloride in powder, and, if used in excess, the solution soon deposits an abundant crystalline precipitate soluble in much water. All so far is as Wicke describes it; but the precipitate, however, is mercuric sodium sulphite, and not, as he supposed it to be, mercuric hydrogen sulphite. The dissolution of the mercuric chloride liberates much sulphur dioxide, which escapes with effervescence when the solution of pyrosulphite is concentrated, as it should be, in order to precipitate the salt. There should be, of course, no liberation of sulphur dioxide if Wicke were right, nor should the crystalline salt yield a large residue of sodium sulphate on ignition as it does. Wicke's salt gave him a bright yellow basic salt when treated with potassium hydroxide. The undissolved crystals may, indeed, give a little *red* mercuric oxide with solution of *sodium* hydroxide of great concentration, but not even that with a solution of potassium hydroxide. Even if the crystals were mercuric hydrogen sulphite, they would not give a basic precipitate with potassium hydroxide, but colourless, neutral, sparingly soluble mercuric potassium sulphite. Only mercuric chloride or its compound with sodium chloride would give a bright yellow precipitate such as Wicke obtained.

What is probably a solution of mercuric hydrogen sulphite is described in the following section.

Mercuric Hydrogen Sulphite Solution.

Three chemists have published observations on the reactions of sulphur dioxide with mercuric oxide in the presence of water—Rammelsberg, Péan de St.-Gilles, and Vogel; all found a white substance take the place of the mercuric oxide, and another mercury compound go into solution, but beyond this their observations do not agree. Rammelsberg found the white substance to be a mercurous anhydrosulphite of varying composition, and the compound in solution to be mercurous sulphate. St.-Gilles states that the solution yielded a precipitate of a mixture of mercuric sulphite and mercurous sulphate, and that until this precipitate had formed it did not contain either a mercurous salt or a sulphate; whilst Vogel found the white substance to be mercurous sulphate, partly soluble in the mother-liquor as a compound not precipitable by common salt (*Watts's Dictionary*; *Gmelin's Handbook*).

We agree with none of these findings as a whole. We hold that neither Rammelsberg's *mercurous anhydrosulphite* nor St.-Gilles' *mercuric sulphite* exists; we find, moreover, that Vogel's white "mercurous sulphate" is really mercurosic sulphite. Coming now to the solution obtained along with the white substance, it certainly contains sulphuric acid from the very first appearance of the white substance, and St.-Gilles is wrong in denying Rammelsberg's statement to that effect. Further, it contains its mercury as mercuric salt, as St.-Gilles and Vogel (?) seem to have held, and not as mercurous salt, as Rammelsberg has stated.

None of these chemists seem to have noticed that mercuric oxide may be dissolved in sulphurous acid without the formation of any precipitate; the conditions for securing such a dissolution of the oxide are, however, simple. The sulphurous acid solution must not contain much sulphuric acid (commonly present as the result of atmospheric oxidation); and the mercuric oxide must be prepared by precipitation, must be added well divided and suspended in water to the sulphurous acid, and only in small quantity, because only a weak solution can be prepared. A solution, the same in every respect, can be obtained by using mercuric oxysulphite in place of mercuric oxide. Mercurosic sulphite and hypomercurosic sulphite can also be used in place of the oxide, but then there is a residue of metallic mercury. An impure solution can be prepared by cautiously adding, in small quantity, a solution of either mercuric nitrate or sulphate, or of mercurous nitrate or solid mercurous sulphate or mercuric oxysulphate to sulphurous acid; with mercurous salts, half the mercury separates insoluble, and with all these salts either sulphuric or nitric acid remains in the solution. Even by the action of a little nitric acid on mercuric sodium sulphite a dilute mercuric hydrogen sulphite solution can be obtained.*

Properties.—The solution reacts as one of mercuric sulphite in sulphurous acid. It is more probable that it contains mercuric acid sulphite than the normal sulphite, and may, therefore, be regarded as a solution of that salt, in absence of any evidence to the contrary. The acid sulphite is the hydrogen double salt, $Hg(SO_3H)_2$, similar to the sodium double salt, $Hg(SO_3Na)_2$, in which the mercury is wholly non-oxylic. Thus constituted, its ready conversion to mercurosic sulphite admits of more satisfactory explanation than if its mercury were half oxylic. The question as to the non-existence of acid sulphites of the alkali metals is not affected by the existence of this specially constituted mercuric salt.

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* See also the account, in the latter part of this section, of the action of sulphurous acid on mercuric chloride.

Unlike the mother-liquor of mercurosic sulphite, the solution of mercuric hydrogen sulphite, when prepared from pure materials, contains no sulphuric acid, moreover, all its mercury is in mercuric combination. Alkalis give no precipitate of mercuric oxide, because they form a soluble double sulphite, precipitable, however, by alcohol. Any specific action on mercurous salts cannot be investigated, because of that exerted on them by the sulphurous acid present in the solution.

Mercuric hydrogen sulphite solution is very unstable, and readily suffers hydrolysis, either wholly or in part—wholly into mercury and sulphuric acid, in part into mercurosic sulphite and sulphuric acid—sulphurous acid remaining free in both cases. The solution deposits all its mercury slowly at common temperatures, but at once when heated, and an equivalent quantity of sulphuric acid remains in solution.* The reaction may be expressed by the equation—

$$H_2O + Hg(SO_3H)_2 = Hg + HO{\cdot}SO_3H + H{\cdot}SO_3H.$$

Partial hydrolysis, by which mercurosic sulphite is formed, is brought about in two ways. Sulphuric or nitric acid, added in small but sufficient quantity, causes it. Secondly, it is caused by adding more mercuric oxide or some mercuroxylic salt (best, a solution of mercuric nitrate or sulphate) to the solution. Whether the addition proves sufficient or not to exhaust all free sulphurous acid is a circumstance which does not affect the precipitation. Success with such different reagents renders it improbable that the hydrolysis depends on any direct reaction between them and the mercuric hydrogen sulphite. The explanation we offer of the change is that it is induced by effecting a state of supersaturation of the solution with mercuric hydrogen sulphite, so that partial hydrolysis occurs and mercurosic sulphite is precipitated. Mercury sulphites are insoluble in dilute nitric or sulphuric acid, and therefore the addition of one of these acids brings about the state of supersaturation which leads to the sudden hydrolysis and precipitation. Mercuric oxide or salts generate more acid sulphite in the solution, and in this way cause supersaturation. According to this explanation, mercuric hydrogen sulphite must be regarded as a salt soluble in a large quantity of water, and hydrolysed by less water.

The result of the hydrolysis of mercuric hydrogen sulphite when it has only proceeded to the extent of separating one-third of the sulphur as sulphuric acid, appears to depend on the difference between oxylic and non-oxylic mercury compounds; the mercuric radicle, Hg, alone can hold the non-oxylic position in a sulphite, the

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* Facts also mentioned by Vogel; but the solution he examined had been produced along with the white substance (mercurosic sulphite), and already therefore contained sulphuric acid.

mercurous radicle, Hg_2, cannot. The mercurous radicle, on the other hand, can hold the oxylic position, provided a mercuric radicle is in non-oxylic relation to the sulphuryl, whilst the mercuric radicle cannot do so, except in the partial and complex way seen in the basic mercuric oxysulphite. Accordingly, the conversion of mercuric hydrogen sulphite to mercurosic sulphite may be represented by the following equation, in which the upper line shows the hydrolysis of a third of the sulphite, and the lower the double decomposition whereby, with the assistance of mercury set free by hydrolysis, two molecules of mercury hydrogen sulphite become mercury sulphite and hydrogen sulphite :—

$$\left.\begin{array}{l} Hg''\vdots(SO_3H)_2 + OH_2 \\ Hg''(\underline{SO_3H})_2 + Hg''(SO_3H)_2 \end{array}\right\} = \left\{\begin{array}{l} \quad H{\cdot}SO_3H + HO{\cdot}SO_3H \\ 2H{\cdot}SO_3H + Hg''(SO_3)_2Hg'_2. \end{array}\right.$$

Mercuric Chloride and Sulphurous Acid.—It is well known that a nearly boiling solution of mercuric chloride is converted by a stream of sulphur dioxide into mercurous chloride, hydrochloric acid, and sulphuric acid. This reaction does not take place at all in the cold, but the two substances are, even then, not indifferent to each other.

Mercuric chloride is very much more soluble in sulphurous acid than in water. The solution on exposure to air rapidly crusts over and also deposits much crystalline precipitate, both consisting of mercuric chloride rendered insoluble by the escape of some of the sulphur dioxide. Mercuric chloride loses its greater solubility in sulphurous acid if much *sulphuric acid* is present, so that the addition of dilute sulphuric acid to the sulphurous solution quickly induces crystallisation of mercuric chloride. When saturated with mercuric chloride, sulphurous acid dissolves much more *mercuric oxide* than it can otherwise do, without yielding an immediate precipitate. Either on standing or on addition of sufficient mercuric oxide, precipitation begins and slowly proceeds, the precipitate being crystalline mercurous chloride. The appearance of this is equivalent to that of mercurosic sulphite, for, as is described in the next section, this sulphite and mercuric chloride at once react yielding mercurous chloride and mercuric sulphite. Sulphuric acid is formed along with the mercurosic sulphite. That the solution slowly decomposes, even when not fully saturated with mercuric oxide, may be accounted for by regarding a solution of mercuric chloride in sulphurous acid as being charged with mercuric hydrogen sulphite, formed by decomposition of some of the mercuric chloride :—

$$HgCl_2 + 2H(SO_3H) = Hg(SO_3H)_2 + 2HCl.$$

As such it will, by dissolving mercuric oxide, become supersaturated with mercuric hydrogen sulphite, through the action of the oxide on the free sulphurous acid, even though still more oxide may be soluble in it, on account of the hydrochloric acid present. Mercuric chloride is also much more soluble in a solution of sodium sulphite or pyrosulphite, and is then certainly converted into mercuric sodium sulphite.

In further support of the belief, expressed in the last paragraph, that mercuric chloride and sulphurous acid partly change into mercuric hydrogen sulphite and hydrochloric acid, it may be pointed out that, according to Sartorious, it is only between 70° and 80°, and in dilute solutions, that mercuric chloride is completely precipitated as mercurous chloride by sulphurous acid: for, in the first place, it is just at that temperature that mercury sulphites suffer hydrolysis, mercuric sulphite then passing into the stage of mercurosic sulphite, from which mercurous chloride would be precipitated by the hydrochloric acid; and, in the second place, too concentrated a solution of mercuric chloride would, in the course of precipitation, charge the water with so much sulphuric acid that it would stop the conversion of the remainder of the mercuric chloride into sulphite, and therefore into mercurous chloride. The action of sodium sulphite on mercuric chloride also supports the above view, for here the precipitation of the mercurous chloride by heat is certainly preceded by the formation of mercuric sodium sulphite (see the sections on "Normal Mercuric Sulphite and Mercuric Sodium Sulphite").

It may be startling to hear of sulphurous acid decomposing mercuric chloride, when sulphuric acid cannot do so, but then it must be remembered that sulphurous acid completely decomposes both the mercury sulphates, as well as the nitrates, into sulphites and free acid.

Mercurous Chloride and Sulphurous Acid.—According to Vogel, mercurous chloride is converted by sulphurous acid into a grey substance, probably a subchloride; we find the action to be exceedingly slight, however. Ordinary calomel becomes a little greyish when suspended in a small quantity of water through which sulphur dioxide is passed; the effect is soon produced, and does not increase during continued contact with the gas: only traces of hydrochloric acid are to be found in the mother-liquor; there are also traces of sulphuric acid, but these would soon be formed in any case in the solution of sulphurous acid. Left for a day in old solution of sulphurous acid, calomel became dark grey, although even then the action was but slight, for very little hydrochloric acid was in solution. In this case, the sulphuric acid which had accumulated in the solution, probably assisted by rendering the calomel slightly soluble. Precipitated mercurous chloride becomes coloured more readily in water containing sulphurous acid, but still only light grey and with the formation of mere traces of hydrochloric acid. The difficulty of getting precipitated mercurous chloride quite free from other salts makes this slight reaction of little significance. We doubt whether there is any reaction at all between true mercurous chloride and sulphurous acid. When mercurous chloride is precipitated by sulphurous acid itself, it is of dazzling whiteness, which is a strange fact, if it is discoloured by sulphurous acid in other cases. (For an account of the behaviour of mercurous chloride with sodium sulphite, see the section on "Hypomercurosic Sulphite," p. 572.)

Mercurosic Sulphite.

Mercurosic sulphite was in the hands of both Rammelsberg and St.-Gilles, without its true nature being recognised by either of them. It is here, for the first time, therefore, described at any length, and with the composition we give to it. It is a well-defined salt, although from its history it might be supposed not to be such.

Properties.—Mercurosic sulphite is obtained in somewhat different states. Prepared by adding mercuric oxide to sulphurous acid solution, it is in lustrous, crystalline particles, which form felted sheets like paper, when drained on a tile till dry. Prepared from a paste of mercuric oxide and gaseous sulphur dioxide, it is not visibly crystalline, but it forms a voluminous precipitate of crystalline habit, is brilliantly white, and, when pressed whilst moist, crepitates like starch. Prepared by reaction between another mercury sulphite and a mercury nitrate or sulphate, it is a voluminous, apparently amorphous precipitate, of a buff colour. It is then not quite pure, indeed, but its colour can hardly be referred to the presence of any coloured impurity. Since mercurous chloride occurs both of a fine white colour and of a pale buff, it seems allowable to hold that mercurosic sulphite may also do so. We have not got the buff-coloured variety free enough from sulphate, for useful quantitative analysis, but its qualitative reactions are those of the white mercurosic sulphite.

Mercurosic sulphite is insoluble in water. Its composition is expressed by the formula $Hg_3(SO_3)_2(OH_2)_4$. It is very efflorescent, and becomes anhydrous in the desiccator. Only when it is crystalline can it be obtained dry, with all the water of composition retained. Rammelsberg found in his red, crystalline cuprosic (or "cuprosocupric") sulphite 2 mols. H_2O, and St.-Gilles in his yellow amorphous cuprosic sulphite, 5 mols. H_2O. Our preparations of mercurosic sulphite, air-dried in hot weather, have shown slightly less than 2 mols. H_2O, and we cannot be certain that our preparation having 4 mols. H_2O had not already effloresced, and lost a fifth mol. H_2O, although we believe it had not.

Mercurosic sulphite is so stable when dry as to be but very little changed after long keeping. In a closed vessel, it gradually darkens in colour, but nearly bleaches again on exposure to the air for some time. The darkening is in all probability due to the formation of a little hypomercurosic sulphite. Slowly in the air, more quickly in a vacuum, it acquires a slight permanent grey colour, due to the presence of a minute quantity of mercury. The slow decomposition of mercurosic sulphate results in the production of mercurous sulphate, metallic mercury, sulphur dioxide, and water, the same products as those produced by heat. Sulphurous acid blackens both mercurous sulphate and mercurosic sulphite by forming hypomercurosic sulphite; hence, no doubt, the partial blackening when the mercurosic sulphite is kept shut up. After blackening and bleaching in the air, the changed sulphite may be somewhat buff-coloured.

Heated dry at a temperature of about 80°, it evolves sulphur dioxide, mercury, and water, and becomes at first black, then grey-white, leaving mercurous sulphate and some of the mercury as a residue; these may be separated by further heating, so as to volatilise the mercury. The blackening may certainly be referred to the formation of hypomercurosic sulphite, and although it is for the time very great, it is only transitory if the heat is maintained. Examined when blackest, the amount of undecomposed sulphite proves to be exceedingly small. It is not probable that hypomercurosic sulphite forms an intermediate product in the decomposition of the mercurosic sulphite; the moist sulphur dioxide no doubt produces it by a secondary action on the undecomposed mercurosic sulphite, or on the mercurous sulphate (see "Hypomercurosic Sulphite," p. 571). The decomposition of mercurosic sulphite by heat is represented by the equations—

$$Hg_3(SO_3)_2 + 2OH_2 = 3Hg + 2SO_4H_2.$$
$$Hg + Hg_3(SO_3)_2 + 2SO_4H_2 = 2Hg_2SO_4 + 2SO_2 + 2OH_2.$$

Some quantitative measurements of this reaction have sometimes proved in close agreement with the equation, and never widely different from it. We have got 61·2, 58·4, 56·1, and 61·9 per cent. of mercurous sulphate. With 2 mols. H_2O retained by the salt used, the calculated number is 62·3 per cent.; with 4 mols. H_2O nearly 60 per cent. The sulphur dioxide was also measured, but as the gas was not dried, the results were only rough approximations. Instead of 8 per cent., 8·6, 7·8, 8·5, and 8·1 were found. The experiments were made with the aid of the Sprengel pump. There are two material sources of loss of mercurous sulphate in such an experiment; the mercurous sulphate is apt to be lost as fume; and the hydrolysis of the sulphite is liable to proceed more rapidly than the action on the remaining sulphite of the sulphuric acid generated by the hydrolysis. A low production of sulphate should be more evident when the water is as much as 4 mols., and this probably accounts for our getting such a low number as 56 per cent. in one case.

Heated with water, it is converted tumultuously into metal and sulphuric acid.* Enough water being present, no mercurous sulphate is produced :—

$$Hg_3(SO_3)_2 + 2OH_2 = 3Hg + 2SO_4H_2.$$

When the salt is heated dry, its decomposition begins in all probability in this way, but is then modified by the reaction between the sulphuric acid and unchanged sulphite, giving mercurous sulphate and sulphurous acid. The non-production of any mercuric sulphate is to be expected, as it is easy to show experimentally the instant conversion of mercuric sulphate to mercurous sulphate by moist mercury.

Potassium hydroxide converts it into mercurous oxide, insoluble, and mercuric potassium sulphite, going into solution—

$$Hg(SO_3)_2Hg_2 + 2KOH = OH_2 + OHg_2 + Hg(SO_3K)_2,$$

the potassium displacing the mercurous but leaving the mercuric radicle.†

Hydrochloric acid at once decomposes it, the products being sulphurous acid and the two chlorides of mercury. When the mercurosic sulphite is buff-coloured, the mercurous chloride from it is of the same colour. No sulphuric acid is produced in this reaction. The preparations of buff-coloured sulphite, however, to start with, always contain a small quantity of sulphate. *Nitric acid and sulphuric acid* in the dilute state are without action on mercurosic sulphite. Stronger acids dissolve it, but the nitric acid scarcely before being strong enough to oxidise the sulphite. *Sulphurous acid* blackens

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* The property was observed by Rammelsberg in what he regarded as mercurous anhydrosulphite, which he prepared in the same way as is here given for preparing mercurosic sulphite.

† Rammelsberg, by similar treatment of the salt prepared by him, obtained very little potassium sulphite. He would seem to have been working then with a preparation mostly mercurous sulphate. According to Watts (*Watts's Dictionary*) he found his salt to "oxidise" rapidly to mercurous sulphate, mercury becoming free. It is material to state that mercury sulphites do not *oxidise* at all: they do become sulphates, but not by uniting with atmospheric oxygen. It is further to be remarked that the salt, viewed as either mercurous anhydrosulphite or mercurosic sulphite, could not well yield metallic mercury in becoming mercurous sulphate by oxidation, because it already contains less than two atoms of mercury to one of sulphur. It is rightly stated to yield mercury by changing into mercurous sulphate, but it does so in the way mentioned in the text.

and decomposes it, dissolving out the elements of mercuric sulphite and leaving hypomercurosic sulphite insoluble for a time, but then also decomposing (see section on "Hypomercurosic Sulphite," p. 567). The presence of sulphuric or nitric acid greatly hinders, and for a time at least altogether prevents the action of the sulphurous acid, a circumstance greatly facilitating the preparation of mercurosic sulphite. The influence of these acids is important, not only in preserving mercurosic sulphite, but also in connection with its production (see the section on "Mercuric Hydrogen Sulphite Solution," p. 554).

The reaction between sulphurous acid and mercurosic sulphite in absence of sulphuric acid, consists in the exchange of non-oxylic hydrogen for oxylic mercury, as expressed in the following equation:—

$$2Hg(SO_3)_2Hg_2 + 2H(SO_3H) = Hg(SO_3)_2Hg_3 + 2Hg(SO_3H)_2.$$

Sodium sulphite solution produces effects similar to those of sulphurous acid, but acts more rapidly than the acid. The mercurosic sulphite is blackened by being converted into hypomercurosic sulphite insoluble, and mercuric sodium sulphite dissolving; here also as with sulphurous acid, the sodium sulphite exchanges its non-oxylic sodium for half the mercury of the oxylic mercurous radicle of the mercurosic sulphite, the other half of this mercury going to form hypomercurosic sulphite with mercurosic sulphite:—

$$2Hg(SO_3)_2Hg_2 + 2Na(SO_3Na) = Hg(SO_3)_2Hg_3 + 2Hg(SO_3Na)_2.$$

The hypomercurosic sulphite thus formed is acted on by more sodium sulphite, becoming mercuric sodium sulphite and free mercury (see the section on "Hypomercurosic Sulphite," p. 569). *Silver sodium sulphite* solution yields mercuric sodium sulphite in solution, all the silver being precipitated if not in excess. The insoluble sulphite is very black, and appears to be a mercury silver sulphite; it is too black for hypomercurosic sulphite, even unmixed with white silver sulphite;* besides, hypomercurosic sulphite at once reacts with silver sodium sulphite. The reaction between the silver sodium sulphite and mercurosic sulphite appears, then, to be expressed by the equation—

$$Hg(SO_3)_2Hg_2 + 4Ag(SO_3Na) = 2Hg(SO_3)_2Ag_4 + 2Hg(SO_3Na)_2,$$

in which mercuric argentous sulphite appears.

Sodium chloride solution added freely produces much black hypomercurosic sulphite, which slowly disappears on digestion. By add-

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* The "silver sulphide" observed by Vogel, and again by Pleischl, to be formed by the action of sulphurous acid and sulphites upon silver salts, must have been argentous sulphite, and not sulphide at all.

ing the sodium chloride gradually, hypomercurosic sulphite is only produced by the first portions. This difference is due to the mercury salts which go into solution by the action of the first portions modifying that of those added afterwards. The final result of the addition of sodium chloride is expressed by the equation—

$$Hg(SO_3)_2Hg_2 + 2NaCl = Hg(SO_3Na)_2 + (HgCl)_2,$$

but the primary action appears to be that of an exchange of sodium for the oxylic mercury, in which only half of this mercury combines with the chlorine, the other half then going to unite with more mercurosic sulphite—

$$2Hg(SO_3)_2Hg_2 + 4NaCl = Hg(SO_3Na)_2 + Hg(SO_3)_2Hg_3 + HgCl_4Na_2.$$

Then, as the quantity of mercuric chloride increases, and the mercurosic sulphite becomes less, all the mercury goes to form mercurous chloride, while any hypomercurosic sulphite previously formed is slowly converted into chloride (see the section on "Hypomercurosic Sulphite"). *Mercuric sodium chloride* acts in the same way as sodium chloride, the mercuric chloride taking no part; it has no action of its own on mercurosic sulphite, but when sodium chloride is present this salt acts first. *Mercuric chloride* solution added, not in excess, produces mercurous chloride and sulphuric acid, all the mercury being precipitated—

$$Hg_3(SO_3)_2 + 2OH_2 + 3HgCl_2 = 3(HgCl)_2 + 2SO_4H_2;$$

but if added at once in excess, much mercuric sulphite goes into solution in the mercuric chloride, and then slowly changes to mercurous chloride and sulphuric acid, as already described under *normal mercuric sulphite*. *Potassium iodide* solution forms a brownish-yellow mercury iodide and a solution of mercuric potassium sulphite. *Mercuric iodide*, *oxide*, *nitrate*, and *sulphate*, and *mercurous nitrate* and *sulphate*, are without action.

Formation and Preparation.—Mercurosic sulphite is formed in reactions between—

(*a*.) *Sulphurous acid*, water, and *mercuric oxide;*
(*b*.) *Sulphurous acid*, water, and *mercuric oxysulphite;*
(*c*.) *Sulphurous acid*, water, and either *mercuric oxysulphate* or solution of *mercuric nitrate*, or solution of *mercuric sulphate;*
(*d*.) *Mercuric sodium sulphite* and either dilute *nitric acid* or dilute *sulphuric acid* (solutions of either *sodium sulphite* or *mercuric sodium sulphite*, and either *mercuric nitrate* or *mercuric sulphate*);

(*e.*) A *warm* solution of *mercuric sodium sulphite* and *mercuric oxide;*

(*f.*) *Mercuric sodium sulphite* and either *mercurous sulphate* or a solution of *mercurous nitrate;*

(*g.*) *Hypomercurosic sulphite* and a solution of either *mercuric nitrate* or *mercuric sulphate.*

a. (I.) Precipitated mercuric oxide made into a thick paste with water is treated with a stream of sulphur dioxide in a vessel immersed in cold water; the paste rapidly thins by dissolution of the oxide, mercurosic sulphite being formed, and gradually increasing in quantity. In this action, the oxide goes through the stage of soluble sulphite in changing into mercurosic sulphite. Excess of sulphur dioxide does no harm. If the mixture is allowed to grow hot, or if too much water has been taken, there will be some blackening of the product during the passage of the gas, due to the formation of hypomercurosic sulphite; there will be blackening also if water is afterwards added to the sulphite and its mother-liquor. The reason of this is that the permanence of the mercurosic sulphite in presence of sulphurous acid is conditional on there being enough sulphuric acid in the solution; this is a bye-product of the reaction, and the addition of water acts injuriously by diluting this acid too much. Just at first, in the preparation, before any sulphuric acid is formed, the sulphurous acid is at once absorbed by the abundant mercuric oxide; at this period of the operation, however, blackening occurs readily, and the vessel should be well agitated until enough sulphuric acid has been generated. Although the mercurosic sulphite can generally be washed with strongly acidulated water without turning grey, it is better to drain the sulphite on a good porous tile; in half an hour or so it will be found to be dry, surprisingly free from sulphuric acid, pulverulent and non-coherent when scraped off the tile, and almost pure.

(II.) Precipitated mercuric oxide in paste is treated with sulphurous acid solution containing a moderate quantity of sulphuric acid. This method of preparation yields the crystalline variety of the sulphite. When drained dry on the tile, it forms glistening paper-like laminæ. It is possible to prepare mercurosic sulphite without blackening it, by the use of sulphurous acid unmixed with sulphuric acid; to ensure success, the mercuric oxide should be in thick paste, and the sulphurous acid concentrated and added gradually with stirring and cooling.

b. Mercuric oxysulphite may be used instead of mercuric oxide in the preceding method of preparation.

c. Mercuric oxysulphate may also be used in place of mercuric oxide in method *a*. Solution of mercuric nitrate, with the least sufficient excess of nitric acid, is a very convenient source of (crystalline) mercurosic sulphite, when treated with sulphur dioxide, either gaseous or in solution. A solution of mercuric sulphate, not too acid, may also be taken.

d. Mercuric sodium sulphite and nitric or sulphuric acid. The sulphite is best used in the solid state, and the suitable quantity of acid added at once. Insufficient acid causes blackening. The reaction is discussed in the section on "Mercuric Sodium Sulphite" (p. 540). Mercuric sodium sulphite and mercuric nitrate form mercurosic sulphite only by secondary reactions due to the nitric acid (see the section on "Mercuric Sodium Sulphite"). Sodium sulphite and mercuric nitrate first form mercuric sodium sulphite and sodium nitrate, and then the mercuric sodium sulphite reacts with more mercuric nitrate. Were it not for the free acid of the mercuric nitrate solution, it should be possible to add the nitrate until all sodium sulphite had become mercuric sodium sulphite, and after that, further addition of nitrate would form mercuric oxysulphite. But the quantity of free acid sufficient to start the formation of mercurosic sulphite is very small, and (neglecting to account for this) the following equation serves to express the result of the change in presence of acid :—

$$3Hg(NO_3)_2 + 3Na_2SO_3 + OH_2 = Hg_3(SO_3)_2 + Na_2SO_4 + 4NaNO_3 + 2HNO_3.$$

e. Mercuric sodium sulphite and mercuric oxide react together as described in the section on this sulphite.

f. Mercuric sodium sulphite and mercurous nitrate yield the buff-coloured variety of mercurosic sulphite.

g. Hypomercurosic sulphite digested in a solution of mercuric nitrate (or sulphate) quickly changes to the buff-coloured variety of mercurosic sulphite. Hypomercurosic sulphite, as prepared, is nearly always mixed with metallic mercury, but this does not remain in the mercurosic sulphite prepared from it, as mercury is remarkably soluble in mercuric nitrate solution.

Chemical Composition.—The action of hydrochloric acid clearly shows mercurosic sulphite to be a sulphite, and both a mercuric and mercurous salt. The mercurous chloride produced could not come from the mercuric chloride because sulphurous acid has no reducing action upon it in the cold. It could indeed be formed by using an insufficient quantity of hydrochloric acid at first, when the sulphurous acid would act on the remaining mercurosic sulphite (supposed here wholly mercuric) and generate hypomercurosic sulphite, which with more hydrochloric acid would give mercurous chloride; but the suggestion of any such action is precluded by the fact that no sulphuric acid is formed by the hydrochloric acid. Further, potassium hydroxide gives mercurous oxide; and sodium chloride gives mercurous chloride. The mercuric chloride formed in abundance by hydrochloric acid, without liberation of mercury, is full proof of its mercuric nature. Not only is it easily distinguished from mercurous sulphate, by yielding mercuric chloride and sulphur dioxide, and not sulphuric acid, but also at once by decomposing in boiling water, not to yield a yellow residue nearly as large as itself, but only grey mercury of exceedingly small volume. Moreover, its appearance is characteristic. The presence of water in it is readily detected by heating it in a tube. The representation of mercurosic sulphite as having one-third of its mercury in non-oxylic union with the sulphuryl, or as having the mercuric and not the mercurous radicle so related is in full agreement with its reactions.

Sulphur and mercury were determined in the usual way, as already described in the section on "Mercuric Oxysulphite." Water was estimated by drying in a vacuum over sulphuric acid; a few hours proved sufficient to remove nearly all the water, but the time in the desiccator was from 20 to 40 hours. A crystalline preparation showed 4 mols. H_2O, but other preparations showed less. These had to be longer on the tile to get them dry, and loss of water by efflorescence took place; efflorescence proceeds so rapidly as to make the salt show loss of weight during the operation of weighing.

I. 0·8005 gram taken for the mercury, and 0·8110 gram for the sulphur determination.

II. 1·4955 grams taken for water.

III. 1·2533 grams taken for water.

IV. 1·2808 grams taken for water, and of the dried salt, 1·1413 grams for sulphur and nercury. All four quantities were taken from separate preparations.

	$1\frac{1}{2}H_2O$.	I.	II.	III.	IV.	$Hg_3(SO_3)_2,4H_2O$.
Mercury ..	76 24	75·94	—	—	72·20	72·12
Sulphur ..	8·13	8·27	—	—	8·04	7·69
Oxygen ...	12·20	—	—	—	—	11·54
Water	3·43	—	3·21	5·03	8·59	8·65
	100·00					100·00

Rammelsberg's Mercurous Anhydrosulphite believed not to Exist.

Rammelsberg states that the mercury sulphite obtained by him, by treating mercuric oxide with sulphur dioxide in the presence of water, had the composition of a mercurous anhydrosulphite—either $(Hg_2SO_3)_2SO_2$ or $(Hg_2SO_3)_3SO_2$. His results are neither very definite nor theoretically very probable, and therefore as we have failed to get in this way any other sulphite than mercurosic sulphite in the solid state—a salt neither anhydrous nor exclusively mercurous—we are convinced that he must, from some cause, have mistaken the nature and composition of the product he obtained.

Hypomercurosic Sulphite.

Oxygenous mercurous salts are blackened by sulphurous acid and soluble sulphites; they are then converted into hypomercurosic sulphite, a well-defined salt, which has hitherto escaped recognition. It was mistaken by Vogel for mercury, notwithstanding its black colour.

Properties.—Hypomercurosic sulphite is a greyish-black amorphous substance, obtained as a voluminous, flocculent precipitate, insoluble in water. It is very unstable in water, but can be preserved dry for a considerable time, without much change. Its composition is expressed by the formula $Hg_4(SO_3)_2OH_2$. Left to itself at common temperatures, it very slowly evolves sulphur dioxide, leaving mercurous sulphate and mercury. The co-operation of moisture is, no doubt, essential to this change, the primary form of which will be hydrolysis into mercury and sulphuric acid, to be followed by reaction between unchanged sulphite and the sulphuric acid. The production of sulphur dioxide and mercury shows the change not to be one of oxidation of sulphite to sulphate by the air. The equation of the change is—

$$Hg_4(SO_3)_2OH_2 = 2Hg + Hg_2SO_4 + SO_2 + OH_2.$$

Heated dry, to a temperature of about 80°, it rapidly undergoes the same change as that which takes place slowly in the air. On heating it gradually in a vacuum, so as to volatilise the liberated mercury, weights of mercurous sulphate were obtained equal to 46·90 per cent. in one case, and 49·86 per cent. in another, calculation requiring 50·72 per cent. for $Hg_4(SO_3)_2OH_2$. These results are satisfactory, when it is considered that sulphuric acid may be carried off with the mercury and water vapour, without acting on the remaining sulphite, the decomposition being a rapid one; and, further, that in consequence of previous hydrolysis during the operation of getting the sulphite dry for use, a little mercury is liable to be already present with the prepared sulphite.

Heated with sufficient water, it is rapidly and tumultuously converted into metal and sulphuric acid:—

$$Hg_4(SO_3)_2OH_2 + OH_2 = 4Hg + 2SO_4H_2.$$

If the proportion of water is so small as to leave the sulphuric acid somewhat concentrated, some mercurous sulphate is also formed, but not otherwise. The production of the sulphate is then due to reaction between unchanged sulphite and the sulphuric acid. We must anticipate here, in order to say in explanation that hypomercurosic sulphite resists the action of rather dilute sulphuric acid. We made an estimation of the mercury and sulphuric acid produced by the hydrolysis of the sulphite, by weighing the former directly and the latter as barium salt. The results, although not obtained under the best conditions, may be given; they were:—Mercury, 82·33 per cent., instead of 81·80; sulphur, 5·23 per cent., instead of 6·54.

Potassium hydroxide solution converts it into mercuric potassium sulphite, which dissolves, and mercurous oxide and mercury which remain insoluble. The decomposition of the sulphite by alkali is expressed by the equation—

$$Hg(SO_2O)_2Hg_3,OH_2 + 2KOH = Hg(SO_2OK)_2,OH_2 + Hg + Hg_2O + OH_2.$$

Hydrochloric acid at once liberates sulphur dioxide, and forms mercuric chloride in some quantity. The insoluble matter only slowly changes from the nearly black colour of the sulphite to a light grey, even with thorough trituration of the whole in a mortar. It then consists of mercurous chloride and a very little free mercury, while the solution contains no more than minute quantities of mercuric chloride. The primary reaction is evidently expressed by the equation—

$$Hg(SO_3)_2Hg_3 + 4HCl = HgCl_2 + 2H_2SO_3 + Hg + (HgCl)_2.$$

The mercury and the mercuric chloride then slowly unite and form more mercurous chloride, as they can be shown experimentally to have the power to do. Possibly a black hypomercurous chloride, Hg_3Cl_2, is one of the primary products, and then acts upon the mercuric chloride:—

$$Hg_3Cl_2 + HgCl_2 = 2(HgCl)_2.$$

Nitric acid and *sulphuric acid*, when dilute, have no action. It only reacts with nitric acid when that acid is strong enough to oxidise it. Its resistance to acids is very striking, and furnishes a ready means of quickly distinguishing it from mercurous oxide. Acid solutions of mercurous salts are instantly precipitated by sulphur dioxide, gaseous, or in solution. *Sulphurous acid* solution decomposes it, producing a solution of mercuric hydrogen sulphite, and a residue of mercury:—

$$Hg(SO_3)_2Hg_3 + 2H(SO_3H) = 2Hg + 2Hg(SO_3H)_2.$$

There is here double decomposition, in which mercury in the oxylic position exchanges with hydrogen into the non-oxylic one. Two-thirds of this oxylic mercury become free, however, because only *mercuric* hydrogen sulphite can exist. The action of sulphurous acid on hypomercurosic sulphite is almost entirely prevented by the presence of some sulphuric acid; but for this, the sulphite could not be prepared in a state at all approaching purity. The same is true of mercurosic sulphite.

Sodium sulphite solution converts it into mercuric sodium sulphite dissolving, and a residue of mercury, the action being similar to that of sulphurous acid. *Silver sodium sulphite* solution takes mercury in place of its silver, all the silver being precipitated, if not in excess. The blackish hypomercurosic sulphite is converted into something still blacker, probably mercuric argentous sulphite. Excess of silver sodium sulphite does not destroy this black matter, or only slowly destroys it. If boiled with water, it yields spongy silver amalgam; and when washed with cold water, it slowly undergoes the same change. The reaction is perhaps—

$$Hg(SO_3)_2Hg_3 + 6Ag(SO_3Na) = Hg(SO_3)_2Ag_4 + 2Ag + 3Hg(SO_3Na)_2.$$

If the silver sodium sulphite is used in excess, and after the reaction, it is diluted with water, it shows a greyish-white turbidity, through the liberation of a minute quantity of silver. Apparently, a very little mercuric argentous sulphite dissolves in the undiluted solution of the other sulphites, and on dilution parts with some of its silver.

Sodium chloride solution produces mercurous chloride, mercuric sodium sulphite, and mercury:—

$$Hg(SO_3)_2Hg_3 + 2NaCl = Hg(SO_3Na)_2 + Hg + (HgCl)_2.$$

Potassium iodide solution converts it into mercurous iodide and potassium sulphite. Then, as in any case would happen, concentrated solution of potassium iodide resolves this mercurous iodide into mercury, and mercuric iodide dissolving as double iodide; but the presence of the potassium sulphite does not appear to affect this decomposition of the mercurous iodide. As stated in the section on mercuric sodium sulphite, alkali sulphites do not act on mercurous iodide as they do on mercurous chloride and mercuric iodide.

Mercuric chloride solution reacts with hypomercurosic sulphite to form mercurous chloride and sulphuric acid:—

$$Hg_4(SO_3)_2 + 2OH_2 + 4HgCl_2 = 2SO_4H_2 + 4(HgCl)_2,$$

but its action takes some time to complete, and the mercurous chloride is at first very grey. When the mercuric chloride is not in excess, the filtered solution of sulphuric acid is free from both mercury and chlorine, but when it is added quickly in excess and at once filtered, a solution is obtained which continues to deposit crystalline mercurous chloride for some time. The reaction is, therefore, similar to that between mercurosic sulphite and mercuric chloride. First, mercuric sulphite (or chloride sulphite) and hypomercurous chloride (or mercury and mercurous chloride) are formed:—

$$Hg(SO_3)_2Hg_3 + HgCl_2 = Hg(SO_3)_2Hg + Hg_3Cl_2(?Hg + Hg_2Cl_2);$$

then mercuric sulphite and water become mercurosic sulphite and sulphuric acid; the mercurosic sulphite decomposes with mercuric chloride, as stated in describing that sulphite; and so the changes follow on until no more sulphite remains. The hypomercurous chloride (or mercury) slowly unites with mercuric chloride to form mercurous chloride, according to the equation given in this section in the paragraph on the action of hydrochloric acid.

Mercuric oxide (precipitated) has no immediate action on moist hypomercurosic sulphite. With the oxide not in excess, the mixture slowly changes to mercurous sulphate and mercury, a result apparently not due to any direct reaction between the two substances. With the oxide in excess, we once got a bright orange-brown mercury oxysulphite; this has not been fully examined. It is at once decomposed by hydrochloric acid in the usual way, but is insoluble in dilute nitric acid; this affords a ready means of removing the excess of mercuric oxide. A little mercurous sulphate was present with it. *Mercuric nitrate* solution rapidly converts it into mercurosic sulphite, becoming itself changed to mercurous nitrate:—

$$Hg(SO_3)_2Hg_3 + Hg(NO_3)_2 = Hg(SO_3)_2Hg_2 + (HgNO_3)_2.$$

As mercuric nitrate readily takes up mercury, the above equation, showing the transfer of one of the three atoms of the hypomercurous radicle to the mercuric nitrate, presents no difficulty. The mercurosic sulphite obtained in this way is always of a light buff colour, instead of white. This colour is characteristic of mercurosic sulphite not obtained by hydrolytic decomposition; for the reaction between mercuric sodium sulphite and mercurous nitrate or sulphate yields it also of this colour. Formed by hydrolytic methods, it is always exceedingly white. *Mercuric sulphate* solution behaves like mercuric nitrate, but in this case the mercurous sulphate formed precipitates and mixes with the mercurosic sulphite. *Mercurous nitrate* solution and *mercurous sulphate* are, as might be expected, inactive. So, too, is *silver nitrate*.

Formation and Preparation.—Hypomercurosic sulphite is formed in reactions between—

(*a.*) *Sulphurous acid*, water, and *mercurosic sulphite* (also *mercuric oxysulphite*);
(*b.*) *Sulphurous acid*, water, and *mercurous sulphate*, or solution of *mercurous nitrate*;
(*c.*) Solution of *sodium sulphite* and *mercuric oxysulphite*;
(*d.*) Solution of *sodium sulphite* and *mercurosic sulphite*;
(*e.*) Solution of *sodium sulphite* and *mercurous sulphate*, or solution of *mercurous nitrate* or *mercurous chloride*;
(*f.*) *Silver sulphite* and solution of *mercurous nitrate* or *mercurous sulphate* in water.

a. Mercurosic sulphite, when treated with sulphurous acid, yields two-thirds of its mercury as hypomercurosic sulphite, the rest dissolving as mercuric acid sulphite. Since mercuric oxysulphite with sulphurous acid yields mercurosic sulphite, it also yields hypomercurosic sulphite. The sulphurous acid must be added to these sulphites gradually and not in excess, as otherwise it will decompose the hypomercurosic sulphite. The blackening of mercurosic sulphite when heated appears to be a case of the reaction between sulphurous acid and mercurosic sulphite.

b. Mercurous sulphate and nitrate are at once decomposed by sulphurous acid, even in presence of dilute sulphuric or nitric acid, into hypomercurosic sulphite and their respective acids. As the mercurous radicle, from the nitrate, cannot hold the non-oxylic relation to sulphuryl, half its mercury goes to form the hypomercurous radicle on the oxylic side:—

$$2(H{\cdot}SO_3H) + 2(HgNO_3)_2 = Hg(SO_3)_2Hg_3 + 4HNO_3.$$

As already mentioned, hypomercurosic sulphite is destroyed, as well as formed, by sulphurous acid, but its destruction takes place only when the solution contains an inufficient quantity of either sulphuric or nitric acid. In preparing the sulphite by this method, the sulphurous acid solution should be mixed with a little sulphuric acid before pouring it into the mercurous nitrate solution or on to the sulphate. Mercurous sulphate and sulphurous acid mixed with a little sulphuric acid, are the best source of hypomercurosic sulphite. The sulphate should not be dense and crystallised, but flocculent, as obtained by precipitation; in presence of sulphuric acid, the sulphurous acid may be added to it in excess. If concentrated sulphurous acid is added gradually and with stirring to the mercurous sulphate in the state of paste, the sulphuric acid can be dispensed with, but as soon as the sulphurous acid is in slight excess, further addition of it must be stopped; it liberates enough sulphuric acid to protect the hypomercurosic sulphite from its further action, provided an excess of it does not too much *dilute* this sulphuric acid; it is safer and simpler, however, to add some sulphuric acid to the sulphurous acid. It is better not to attempt to purify the sulphite by much washing, as it begins at once to suffer hydrolysis by treatment with water; draining in a thin layer on a good porous tile is the best way, and leaves mere traces of sulphuric acid. The preparation must not be grey, even when dry, but almost black, and in the moist state must not be clotted; clotting and grey colour are proof of hydrolysis having proceeded to some extent.

c. The formation of hypomercurosic sulphite from mercuric oxysulphite by sodium sulphite is somewhat obscure in nature, and has already been described. The amount of hypomercurosic sulphite produced is proportionately small, but is certainly not dependent on the presence of mercurous sulphate before addition of the sodium sulphite.

d. The conversion of mercurosic sulphite to hypomercurosic sulphite by sodium sulphite is quite similar to that which happens when sulphurous acid is used. The sodium sulphite must not be added in excess.

e. Sodium sulphite added to either moist mercurous sulphate or a solution of mercurous nitrate, produces its effect by double decomposition, but as the mercurous radicle cannot hold the non-oxylic position in a sulphite, half its mercury is left to unite with the oxylic mercurous radicle, and convert it into the hypomercurous radicle:—

$$2Na(SO_2ONa) + 2(HgNO_3)_2 = Hg(SO_2O)_2Hg_3 + 4NaNO_3.$$

The sodium sulphate solution should be dilute and be added gradually, but not in excess, as it then rapidly attacks the hypomercurosic sulphite. It is difficult, however, to avoid having a temporary excess of the sodium sulphite, particularly when working with mercurous sulphate; and the process is, therefore, very inferior to that in which sulphurous acid is used, if a nearly pure sulphite is desired. In the case of mercurous chloride, it is hardly possible to go nearer to success than seeing the blackening effect of the sulphide upon the chloride.

f. Silver sulphite can be used effectively as a means of producing hypomercurosic sulphite from mercurous nitrate and even from mercurous sulphate. The insolubility of silver sulphite is so great that it can remain for a few moments in the solution of mercurous nitrate before beginning to lose its whiteness; when started, however, the change proceeds rapidly and soon becomes complete if the mercurous nitrate is in excess. In working with mercurous sulphate, the two salts require intimate trituration with water for some time. The blackening that occurs shows how fully they act on each other, but the hypomercurosic sulphite and silver sulphate can, of course, not be separated. The reaction between mercurosic sulphite and silver sodium sulphite has already been described.

Chemical Composition.—Although hypomercurosic sulphite is produced by the reaction between other sulphites and mercurous salts, its behaviour with reagents shows that it is not a mercurous salt, for it always yields a mercuric compound, as well as mercury and a mercurous compound. Its reactions with hydrochloric acid and with mercuric chloride seem to leave its constitution as a mercuric hypomercurous salt beyond doubt. The mercuric chloride and mercury formed in this case, if well shaken together, combine almost completely and become mercurous chloride.

That in its formation from mercurous nitrate or sulphate, the mercury of two mercurous radicles becomes distributed as a mercuric and a hypomercurous radicle, is in agreement with what takes place on adding excess of sodium or hydrogen sulphate, as then mercuric sodium or hydrogen sulphite and mercury are the products. Evidence of the existence of other hypomercurous compounds is not altogether wanting. Mercury shaken with mercuric chloride solution yields a nearly black precipitate, which is slowly converted into white mercurous chloride by contact with more mercuric chloride. Finely divided mercury is, of course, far removed from black in colour, but if, in spite of this, it should be contended that the black substance may be mercury only, it will be enough, perhaps, to point out for reply that Vogel mistook hypomercurosic sulphite for *mercury in the state of a black-grey powder* (*Gmelin's Handbook*, **6**), when he saw it produced by the action of sulphurous acid on mercurous nitrate.

The reactions of hypomercurosic sulphite are clearly those of a sulphite. Heated in a tube it yields water. Its insolubility in dilute nitric acid at once distinguishes it from mercurous oxide. Its colour distinguishes it from other mercury sulphites, and also from grey lustrous mercury, into which it so quickly changes, under conditions similar to those in which it is formed. From mercury it is also distinguished in being flocculent and voluminous. Its behaviour, when heated, either wet or dry, has already been described as evidence of its quantitative composition.

Dissolved in a mixture of bromine and hydrochloric acid, and precipitated by the usual methods, it has given us the quantities of mercury and sulphur tabulated below. Water has not been directly determined, because sulphur dioxide is also evolved in the desiccator.

The weights taken for analysis were 0·8073 and 1·2510 grams of different preparations.

	I.	II.	$Hg_4(SO_3)_2,OH_2$.
Mercury	81·55	81·95	81·80
Sulphur	6·50	6·44	6·54
Oxygen........	—	—	9·82
Water	—	—	1·84
			100·00

General Constitution of the Mercury Sulphites.

The reactions, formation, and composition of the mercury sulphites seem to establish the five propositions which follow concerning their general constitution.

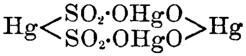
1. In mercury sulphites, the relation of basic to acid radicle is of two kinds; it is half like that of the basic element in oxylic salts (such as sulphates and nitrates), and half like that of the basic element in salts of the halogens, including cyanogen.

2. The mercuric radicle, Hg, takes up and preserves the non-oxylic relation to sulphuryl, with an energy to be compared to that it exerts in its cyanide and iodide. This is the central conception in the chemistry of the mercury sulphites, for without it all peculiarities stand unexplained.

3. The mercurous radicle, Hg_2, never holds non-oxylic relation with sulphuryl, and when presented in chemical reactions to a sulphite, resolves itself into the mercuric radicle which goes to the sulphuryl, and mercury which becomes free or changed into the hypomercurous radicle, Hg_3.

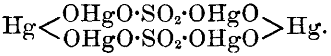
4. The mercuric radicle, in presence of water, can hold the oxylic relation to sulphuryl in such an imperfect way only, that two-thirds of it are in combination with simple oxygen radicles. But two such compounds are known, both of which have exclusively the mercuric radicle for base, namely, mercuric oxysulphite and mercuric oxysulphate:—

Oxysulphite.



$$Hg{<}{\begin{matrix}SO_2{\cdot}OHgO\\SO_2{\cdot}OHgO\end{matrix}}{>}Hg$$

Oxysulphate.

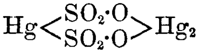


$$Hg{<}{\begin{matrix}OHgO{\cdot}SO_2{\cdot}OHgO\\OHgO{\cdot}SO_2{\cdot}OHgO\end{matrix}}{>}Hg.$$

The oxysulphite presents itself as a combination at once stable and unstable; for while its formation actually involves the liberation of nitric acid from a nitrate, as well as its insolubility in this acid when dilute, yet it is afterwards exceedingly liable to decomposition. Its formation in circumstances, the like of which would prevent that of any other basic salt, seems due to the energy with which the mercuric radicle and sulphuryl enter into non-oxylic union, the sulphuryl being then compelled to take up other mercuric radicles on its oxylic side, in order to complete the salt. It is the feeble hold of sulphuryl on the mercuric radicles in oxylic union with it, which then, in conjunction with the readiness of the sulphites of mercury and of silver to undergo hydrolysis, gives to this sulphite its great instability.

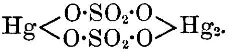
5. The mercurous radicle can enter into oxylic union with sulphuryl, but only when this is exclusively united with mercury as base. Mercuroso-mercuric sulphite and mercurous sulphate are, therefore, the only mercurous salts, no double mercurous sulphates being known:—

Mercurosic sulphite.



$$\mathrm{Hg}{<}\begin{matrix}\mathrm{SO_2{\cdot}O}\\ \mathrm{SO_2{\cdot}O}\end{matrix}{>}\mathrm{Hg_2}$$

Mercurous sulphate.



$$\mathrm{Hg}{<}\begin{matrix}\mathrm{O{\cdot}SO_2{\cdot}O}\\ \mathrm{O{\cdot}SO_2{\cdot}O}\end{matrix}{>}\mathrm{Hg_2}.$$

The Nature of Reduction by Means of Sulphurous Acid.

In describing the formation and changes of mercury sulphites, most of what we wish to say about the reduction of mercuric to mercurous salt, and of the latter to metal by sulphurous acid, has already in a manner been said. The subject is, however, of such interest and importance, and the nature and course of the reduction has hitherto been so superficially or so erroneously apprehended, that a section of this paper may well be devoted to giving a connected statement of what we have made out about it.

When sulphurous acid or a sulphite effects the reduction of mercury or silver, or reduces ferric to ferrous salts, thereby becoming sulphuric acid or sulphate, *it is not really the case that the sulphurous acid is, as such or directly, oxidised by the metallic salts*, either immediately, or, in the case of haloïd salts, through the intervention of water. As an expression of the result of heating sulphurous acid with mercuric chloride, the following equation is of course true, and for its purpose is free from objection:—

$$H_2SO_3 + OH_2 + HgCl_2 = H_2SO_4 + 2HCl + Hg.$$

But it is wrong if the implication is intended that the sulphurous acid and the mercuric chloride make a combined attack upon water, and share its elements between them, the truth being that they first attack each other (see the section on "Mercuric Hydrogen Sulphite").

In most cases certainly, and probably in all, the first step in the reduction is the formation of a sulphite of the metal with its combining value undiminished. Mercuric salts yield mercuric hydrogen sulphite, mercuric sodium sulphite or other double salt, mercuric oxysulphite, or mercuric sulphite combined with chloride. According to

Berzelius, mercuric selenite and sulphurous acid become mercurous selenite and sulphuric acid, but this is a mistake, the sulphurous acid displaces the selenious acid, and the mercuric sulphite suffers hydrolysis into mercurosic sulphite and sulphuric acid. With excess of sulphurous acid, the selenium is slowly precipitated from solution and colours the mercurosic sulphite, thus making it look a reducing selenite and liable to cause a mistake: mercurous selenite is not formed. Mercurous sulphite is unknown, but mercurous salts yield hypomercurosic sulphite metameric with it (see the previous section). Silver nitrate, sulphate, chloride, or oxide, treated with sodium sulphite become either silver sulphite or silver sodium sulphite, and the nitrate and sulphate become sulphite when treated with sulphurous acid. The reddening of ferric solutions on the addition of sulphurous acid as well as of sodium sulphite, precedes reduction, and this indicates the formation of ferric sulphite, for a similarly coloured solution is obtained by dissolving ferric hydroxide in sulphurous acid, and this has the properties of a solution of ferric sulphite. Dilute sulphuric acid or nitric acid does not prevent the formation of sulphites; and when from the presence of one of these acids in greater concentration this formation is prevented, so also is reduction. Sulphurous acid has scarcely any action on mercurous or silver chloride, perhaps none if sulphuric acid and other impurities are altogether absent; so that here, too, absence of reduction goes with non-formation of sulphite. It does reduce mercuric chloride, and here apparently also forms sulphite (see section on "Mercuric Hydrogen Sulphite").

A sulphite being formed, metal becomes reduced from it in one of two ways. Mercurosic and hypomercurosic sulphites treated with sulphurous acid or sodium sulphite are resolved into free mercury and mercuric sulphite, dissolving as double salt of hydrogen or sodium. The consequence is remarkable, for it follows from this that mercury may become metal without oxidation of any sulphurous acid or sulphite radicle whatever; thus (ignoring the intermediate formation of hypomercurosic sulphite) the reaction between mercurous chloride (or nitrate) and sodium sulphite, and that between mercurous nitrate and sulphurous acid are expressed by the equations—

$$(HgCl)_2 + 2Na(SO_3Na) = Hg + Hg(SO_3Na)_2 + 2NaCl$$
$$(HgNO_3)_2 + 2H(SO_3H) = Hg + Hg(SO_3H)_2 + 2HNO_3.$$

Such reactions can hardly be regarded as cases of reduction, half the metal drops out in the interaction of the substances, just as it does when potassium iodide acts on mercurous iodide. They might, with as little impropriety, be treated as cases of *oxidation* by a sulphite, since a mercuric is got from a mercurous salt.

The other way in which reduction of metal is brought about is by hydrolysis, or an equivalent change. Water converts the sulphite into metal and sulphuric acid. The hydrolysis proceeds in stages, usually apparent:—

$$\begin{aligned}6Hg_2(SO_3)_2 + 4OH_2 &= 4Hg_3(SO_3)_2 + 4SO_4H_2\\ 4Hg_3(SO_3)_2 + 2OH_2 &= 3Hg_4(SO_3)_2 + 2SO_4H_2\\ 3Hg_4(SO_3)_2 + 6OH_2 &= 12Hg + 6SO_4H_2.\end{aligned}$$

But this is unimportant here, since the stages are alike in the nature of the reduction, and the reactions of the several sulphites may be said to prove that mercury each time becomes free, but then unites with unchanged salt so as to build up the mercurous and hypomercurous radicles. Ferric sulphite apparently does not suffer hydrolysis, but still it becomes reduced to ferrous sulphite by the iron losing one-third of its hold upon the sulphite radicle. There is nearly the same separation between metal and sulphite radicle as occurs when mercuric sulphite becomes mercurosic sulphite by hydrolysis, but the acid radicle is differently disposed of. According to Gélis, the red solution of ferric hydroxide in sulphurous acid is a solution of ferric sulphite, and slowly suffers, in absence of other acid or of air, conversion into ferrous sulphite and ferrous hyposulphate.

But ferrous hyposulphate is equivalent to ferrous sulphite combined with sulphuric oxide, and when boiled with an acid it yields sulphate; in this way the ferric sulphite becomes ferrous sulphite and sulphuric acid.

Hydrolysis therefore is equivalent to oxidation of sulphurous acid to sulphuric acid by reduction of mercury, silver, or ferric compounds; but in nature it is the displacement of metal by the hydrogen and hydroxyl of water, in which process hydrogen takes the place of the metal, and oxygen converts its half haloïd into wholly oxylic union with the sulphuryl. It will be seen that reduction by hydrolysis of the sulphites is a process the reverse of that of the separation of metal by the action of sodium or hydrogen sulphite. In the latter, mercurous becomes mercuric salt by part of the mercury dropping out of combination with the sulphite radicle; in the former, when part only of the sulphite radicle is separated from the mercury of the water, mercuric becomes partly mercurous or hypomercurous salt.

The Oxidation and Hydrolysis of Sulphites as Evidence of their Constitution.

Mercury and silver sulphites are not liable to atmospheric oxidation. In this respect, they resemble organic sulphites (sulphonates), and differ from most inorganic ones. There seems no reason why they should be so if sulphites are dioxylic salts of thionyl, $(AgO)_2SO$; but when sulphites are regarded as having a hemi-haloïd constitution, the explanation at once suggests itself.

In forming a sulphite with sulphur dioxide, a basic oxide becomes half deoxidised, just as it does when it unites with chlorine, except that with this it gives a haloïd salt and an oxylic salt, whereas with sulphur dioxide it gives but one salt, hemi-haloïd, hemi-oxylic, because here, simply, the acid radicle is bivalent. Thus conceived, a sulphite possessing, as it does, half-deoxidised metal, is liable to direct oxidation according as its metal is readily oxidisable or not. The ready hydrolysis of the sulphites not liable to oxidation serves to show that sulphuryl prefers dioxylic union with metallic radicles to the half-haloïd union with them it has in sulphites; it is therefore ready in all sulphites for union with more oxygen, but when the sulphite is of mercury or silver it cannot directly* take up oxygen because of the indifference of the metal.

Chlorides, to which in illustration reference has just been made, do not oxidise, because their haloïd radicle has a characteristic preference for direct or non-oxylic union with metals; their basic radicle, however, does in some cases oxidise at elevated temperatures, their chlorine then becoming free. (This aspect of varying oxidisability of haloïd salts is further noticed in the section on the "Relation of Selenites to Sulphites.")

On the assumption that sulphites are thionyl compounds, there is no way of accounting for the hydrolysis of some of them. Water would have to be decomposed by the sulphite into its elements, its oxygen going to the thionyl, and its hydrogen taking up oxygen again (!) by displacing mercury or silver; or the sulphite would have first to be changed by hydrolysis into basic oxide and sulphurous acid or oxide, and then the latter act reducingly on the basic oxide. Neither of these interpretations of the nature of the change is probable. It will therefore be sufficient to point out again, in connection with the second, that on trial sulphurous acid does not become oxidised by mercury oxide, but combines with it to form a mercuric sulphite. Hydrolysis may be regarded as a test of the constitution of an oxygenous salt; if it yields acid and basic oxide, or hydroxide, the

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* "Directly," that is, as regards the argument in the text, although Traube's view of atmospheric oxidation is most likely true here, as in other cases:

$$\left.\begin{matrix}Na\\NaO_3S\end{matrix}\right\} + OH_2 + O_2 = \left.\begin{matrix}Na\\NaO_3S\end{matrix}\right\}O + H_2O_2.$$

In the report of the Inventions Exhibition by the editor of the *Journal of the Society of Chemical Industry*, Messrs. Boake and Co. are said to have exhibited potassium metasulphite (pyrosulphite) having the advantage of not being liable to oxidation. This property will of course be lost in presence of moisture.

salt is wholly oxylic; if it yields acid and metal (hydrogen or hydrocarbon), the salt is partly haloïd.

Sulphites resemble Chlorides, Iodides, and Cyanides in Properties.

Mercury and silver sulphites possess certain properties which are of value as indications of the partly haloïd character of their acid radicle, because they belong more or less fully to haloïd as distinguished from oxylic salts. Such properties are, that of decomposing in ways equivalent to a separation of the metal from the salt radicle; relative insolubility in acids; and that of forming double salts when possible.

Silver and Mercury Sulphites Decompose much in the same way as some Haloïd Salts.—Mercuric sulphite is unlike any purely oxylic salt, and resembles many haloïd salts, in yielding up a third or a half of its chlorous radicle, and thus becoming mercurosic or hypomercurosic sulphite. Thus, manganese tetrachloride becomes a lower chloride by giving up a quarter or a half of its chlorine; cupric and ferric iodides become cuprous and ferrous by setting free some of their iodine; cupric cyanide becomes cuprous by parting with cyanogen, and so in other cases. Again, much as these sulphites become metal and sulphuric oxide in hot water, gold chlorides by a moderate heat become metal and chlorine. The differentiation of a sulphite from a purely oxylic salt is here perfect, and although its resemblance to a simple haloïd salt is not complete, the conditions of its decomposition being unlike those of a haloïd in including the presence and activity of water, there is good reason for this in the consideration that the sulphite is half oxylic in constitution, and consequently requires the assistance of water in decomposing.

The Comparative Insolubility of Silver and Mercury Sulphites in Acids.—Before trying to show the significance of this fact, it may be well to point out, more distinctly than is done in Gmelin's or other handbooks, the extent of the insolubility of silver sulphite.

Silver nitrate solution is copiously precipitated by sulphurous acid. The reaction is immediate, and so certain that silver nitrate solution proves as sensitive to either gaseous or dissolved sulphur dioxide as lime-water is to carbon dioxide, whilst the brilliant whiteness of the silver sulphite makes the effect much more visible than the lime-water effect, and thus well fitted for class demonstrations, and as a test for sulphur dioxide. Except when the silver nitrate is in concentrated solution, the precipitation of silver is almost complete. Nitric acid is, of course, liberated in this reaction, and so insoluble is silver sulphite in this acid as to be hardly affected until the acid is strong enough to oxidise it and become itself reduced to nitrous fumes. Excess of sulphurous acid has no action on the precipitate, for a time at any rate, in presence of the nitric acid which has been set free.

Silver sulphate is quickly converted by sulphurous acid into silver sulphite and sulphuric acid. On the other hand, sufficiently concentrated or hot dilute sulphuric acid decomposes the sulphite, reversing the change.

The great insolubility of mercurosic and, above all, hypomercurosic sulphite, in nitric acid, and even sulphuric acid, is noticed in other sections of this paper; and so is the behaviour of mercuric oxysulphite towards acids, but this it will be well to describe again in the present connection because of its significance. Although a basic salt it, like the other sulphites, is insoluble in rather dilute acids, as might indeed be expected from the fact of its formation being attended with liberation of nitric acid. When it does dissolve in stronger acid, it does so with little or no liberation of sulphur dioxide; the solution, indeed, changes rapidly, and mercurous sulphate is the result, but if, without delay, hydrochloric acid is added to the solution, very little mercurous chloride is precipitated, and abundance of sulphur dioxide is given off—effects which show that the sulphite *dissolves as such*. Hence it will be seen that the insolubility of mercury and silver sulphites is not, in some way or other, a *cause* of their not being decomposed by acids, but a *result* rather of their resisting decomposition.

To come now to the interpretation of this resistance of silver and mercury sulphites to the action of oxylic acids, as evidence that sulphites have the character of haloïd salts. In the first place, if these sulphites were simply oxylic salts they would be the only oxylic salts of silver and mercury insoluble in dilute nitric acid, the sulphates in part excepted; while as haloïd salts they are far from exceptional in this respect. Stronger acids decompose them, and so does strong sulphuric acid decompose, to some extent, mercury haloïd salts. The action of nitric acid on silver sulphite is the same as on silver cyanide (except that it is more easily exerted than on the latter), these salts being unchanged by cold dilute acid, and decomposed with deoxidation of the nitric acid when this is hot and strong.

In the second place, if sulphites had to be ranked simply as oxylic salts, it would be incomprehensible that silver and mercury sulphites should be insoluble in dilute *sulphuric* acid, and be freely formed from the *sulphates* by sulphurous acid. For sulphurous acid not only proves to be much weaker than sulphuric acid in salts of other metals, but as the elements of the two acids are the same, the acid with more oxygen should be the stronger acid. As haloïd salts, on the other hand, silver and mercury sulphites are not peculiar, since, as every one knows, not only do the strong haloïd acids decompose silver and mercury sulphates, but so also does hydrogen cyanide, feeble as it is towards alkalis. Sulphites, as haloïd salts, have an essentially different constitution from that of sulphates, half their metal being directly united to the sulphur of sulphuryl; so that mercury and silver sulphites form and exist in the presence of sulphuric acid, for much the same reason that mercury mercaptide proves to be a very stable body, although mercury ethoxide cannot even exist.

The Stability of the Double Sulphites resembles that of the Double Cyanides, Iodides, and Chlorides.—A reference to the section on "Mercuric Sodium Sulphite" will show how this salt resembles the corresponding iodide and cyanide, in the circumstances under which it forms, and in its behaviour to reagents. Silver sodium sulphite is but little behind the mercury salt in this respect. Sodium hydroxide and chloride do not precipitate the silver from the double salt, whilst silver oxide, chloride, and other salts of silver dissolve in sodium sulphite.* The double sulphites, like the double cyanides, are neutral to litmus, although alkali cyanides and sulphites are strongly alkaline.

Plainly in the matter of forming double salts, sulphates resemble haloïd salts. Many oxylic salts do indeed form double salts, but not under such conditions as those in which the mercury and silver double sulphites can form. These wholly oxylic double salts are able to resist little more than the action of water, and appear to be held together mainly by forces of crystallisation only. Such salts of mercury and silver are but little known, and are decomposable even by water.

In the same way that sulphites resemble haloïd salts they are like thiosulphates, in which also the metal is half oxylic—$AgS{\cdot}SO_2{\cdot}ONa$. Hyposulphates, so closely related to sulphites in origin, show no relation to haloïd salts; they are wholly oxylic—$(SO_2ONa)_2$.

The Constitution of Sulphites a Clue to that of Cyanides and other Halides.

The simple halogens, and cyanogen, like the radicle of the sulphites, form double salts of a little oxidisable metal and a highly oxidisable metal, which are more stable than their salts, formed exclusively of one or the other kind of metal. It seems clear that this two-sided character of the sulphite radicle in its combination with metals is due to its constitution, through which it acts half as an oxylic radicle. But, this being the case, the halogens should owe their two-sided character as acid radicles also to peculiarities of constitution. Cyanogen is a compound radicle, and admits of being dealt with from this point of view. Chemists are not decided as to whether

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* This was pointed out in a previous paper by one of us last year. Captain Abney has recently recommended the use in photography of sodium sulphite, in place of thiosulphate.

cyanides are carbamines or nitriles; more commonly they are represented as the latter, but there is much to be said in favour of their being carbamines, as pointed out by one of us in a previous paper (Trans., 1885, 227). Now by giving them a constitution half-carbamine, half-nitrile, an explanation is afforded of their remarkable tendency to be double salts. Writing them thus—

Potassium cyanide.	Silver potassium cyanide.
$\mathrm{KN\vdots C\vdots N\vdots CK}$	$\mathrm{AgN\vdots C\vdots N\vdots CK}$,

with half their metal united to nitrogen and half to carbon, it would seem certain that silver or mercury, from its affinity for nitrogen, would form a more stable combination than potassium on the nitrogen side of the cyanogen, and will not do so on the carbon side.

The stability of mercury potassium iodide is no less remarkable than that of the cyanide or sulphite, although in it the chlorous radicle is a simple halogen. When hydrogen iodide is put in contact with a mixture of potassium hydroxide and mercuric oxide, it does not take one and leave the other, but satisfies itself half with one and half with the other. It would, therefore, seem that in $\mathrm{Hg(I_2K)_2}$, the group $\mathrm{I_2}$(or $\mathrm{I_4}$) has a structure, constitution, or internal relation of parts, by which it presents to basic radicles two forms of combining power. Why should it not? Turning to a kindred matter, well before the attention of chemists, we will reply by another question. Which, we would ask, is more probable: that the resemblance of the periodic series of the elements to the homologous and isologous series of organic compounds is a chance one; or that it is due to the elements being themselves complexes?

NOTE ON THE CONSTITUTION OF FULMINATES, BY EDWARD DIVERS.—It will be seen that the matter of the section to which this note is appended, bears on the question as to the nature of the fulminates, since they show so marked a difference in their two units of basicity. I hope yet to publish again on their formation and constitution, as some work now going on in my laboratory, on mercury and nitric acid, promises to throw light on the matter; but in the present connection I wish to point out a modification of the formula I have proposed for a fulminate, which, without much altering its general significance, would make it fulfil two desirable ends. Instead of $\mathrm{AgO\overline{CNONC}Ag}$, I would write $\mathrm{AgOC\underset{Ag}{N}ONC}$, that is, remove Ag from C to an N, disconnect the Cs, and read the Cs and Ns with valencies the same as they have in carbamines, either $\mathrm{C''}$ and $\mathrm{N'''}$ or $\mathrm{C^{IV}}$ and $\mathrm{N^{V}}$. Thus, first, the advantage is gained of representing the carbons disconnected, in accordance with the evidence afforded by the action of chlorine and iodine on the fulminates (Trans., 1885, 78), that fulminates do not yield dicarbon compounds; and, secondly, of having the silver atom which is not displaceable by potassium standing in union with nitrogen instead of carbon. I have always felt the disconnection of the silver from the nitrogen to be a weak point in my formula, but, as stated in my first paper on the subject (Trans., 1884, 22), the supposed formation of fulminates from nitrous acid and alcohol make this disconnection difficult to allow. This formation having since then been disproved by Mr. Kawakita and myself (*loc. cit.*, 27), the difficulty it caused is removed; and now the study of mercury sulphites further inclines me to assign to the mercury or silver in a fulminate a direct connection with nitrogen, as in the modified formula given above.

Sulphur, Selenium, and Tellurium Sulphoxides are Sulphites.

In this Journal (Trans., 1885, 218, and in earlier papers, in conjunction with Mr. Shimosé), one of us has given to the compounds which sulphuric oxide forms with sulphur, selenium, and tellurium, formulæ like this: $O_2S\overset{O}{\diagup\!\diagdown}Te{=}Te\overset{O}{\diagup\!\diagdown}SO_2$, in which the element is represented as having gone half into direct union, half into oxylic union with the sulphuryl. Now, doing this makes them sulphites in constitution, and such they must apparently be taken to be.

They are hydrolysed by water partly into sulphurous acid and what is equivalent to a base:—

$$Se_2(SO_3)_2 + 2H_2O = (Se + SeO_2) + H_2SO_3.$$

They are also partly hydrolysed, like silver sulphite, into metal and sulphuric acid:—

$$Te_2(SO_3)_2 + 2H_2O = 2Te + 2H_2SO_4.$$

They stand in the same relation to the sulphites of strong metals as the corresponding chlorides do to metal chlorides. They resemble salts of the halogens in some of their relations. They are not only formed by the direct union of their quasi-metal with the sulphur trioxide, but can to a certain extent be decomposed again into these by heat in a vacuum; thus, the selenium compound (Trans., 1885, 203), decomposes much as platinous chloride does:—

$$Se_2(SO_3)_2 = 2Se + (SO_3)_2 \qquad Pt_2Cl_4 = 2Pt + 2Cl_2.$$

The selenium compound, like the chlorides of selenium, dissolves in fuming sulphuric acid without decomposition. When thus dissolved, it is decomposed, like a sulphite, by hydrochloric acid:—

$$Se_2(SO_3)_2 + 2ClH = Cl_2Se_2(SO_3) + SO_3H_2,$$

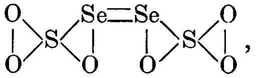
and this compound, not yet isolated (*loc. cit.*, 195), reacts with more hydrochloric acid, just as the corresponding chloride sulphite of mercury (section of this paper on "Mercurosic Sulphite") does with water:—

$$Cl_2Se_2(SO_3) + ClH = Cl_2Se_2 + ClHSO_3$$
$$Cl_2Hg_2(SO_3) + (HO)H = Cl_2Hg_2 + (HO)HSO_3.$$

Admitting these compounds to be sulphites, a further illustration that sulphites resemble haloïd salts is seen in their formation direct from metal and sulphuric oxide:—

$$2Te + (SO_3)_2 = Te_2(SO_3)_2.$$

In a previous paper by one of us, these compounds have been treated as substitution representatives of sulphuric peroxide, SO_4, thus:—



and such they remain when regarded also as sulphites; for just as hypochlorous oxide may be regarded as chlorine hypochlorite, so may sulphuric peroxide (if SO_4 expresses its composition), be regarded as oxygen sulphite,  $O\langle O \rangle SO_2$, or the compound $ClHSO_3$ as chlorine hydrogen sulphite, $\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2$, which in reactions it proves to be.

NOTE BY E. DIVERS ON SULPHURIC OXIDE.—In the paper on "The Constitution of some Non-saturated Oxygenous Salts" I was led to discuss the constitution of sulphuric oxide. I pointed out the strong probability there is of this oxide being *sulphuryl sulphate*, and in a more recent paper, in conjunction with Mr. Shimidzu, I gave further experimental evidence in favour of this view. I would now make good an omission in not calling attention to a synthesis of sulphuric oxide, effected many years ago by Odling and Abel (*Chem. Soc. J.*, **7**, 2), which leads to the adoption of the same view. Sulphuryl bromide and silver sulphate heated together yield silver bromide and sulphuric oxide:—

$$(SO_2)Cl_2 + Ag_2SO_4 = (SO_2)SO_4 + 2AgCl.$$

In using the name *sulphuryl sulphate*, it is not suggested that there is any difference in the two sulphur-atoms, sulphuryl sulphate being neither more nor less than sulphuryl oxide doubled:—$[O_2S : O_2 : SO_2]$.

The Relation of Selenites to Sulphites.

With the exception of a few unstable compounds, all sulphites have the hemihaloïd or sulphonic constitution. It may be otherwise with selenites in consequence of the more basylous character, yet, on the whole, much weaker combining power, of selenium; and dioxylic selenites may be the common form.

Ethyl selenite is dioxylic and easily prepared; ethylselenonic acid or ether is unknown. The existence of methylselenonic acid is not certain, for Wöhler and Dean's results are not conclusive on this point.

Metallic selenites are generally considered to have a family resemblance to sulphites; or, perhaps, it would be more correct to say that they are *assumed* to have it. If they really are like sulphites, then they cannot but have the same constitution, but if they are not like sulphites they may differ in constitution and be dioxylic. They do exhibit many unlikenesses to sulphites, but these are hardly such as would suggest that the selenites differ from the sulphites in being dioxylic. Their differences are, rather, such as may be attributed to selenious acid being a more condensed acid than sulphurous acid, and to the feebler affinities of selenium. If, though hemihaloïd, selenites do not oxidise in the air like sulphites, that is only because for oxidation to take place it must proceed simultaneously on the metal and on the chlorous radicle: therefore, because of the selenium, sodium selenite does not oxidise; and because of the silver, silver sulphite does not; whilst sodium sulphite does oxidise because the sodium and sulphur take the oxygen between them. (See, further, the section on the "Oxidation of Sulphites.")

Among the undoubted resemblances of selenites to sulphites, are some of those peculiarities which distinguish sulphites from oxygenous salts generally, and connect them with haloïd salts. Mercury and silver selenites have a degree of insolubility in nitric acid which, though less than that of sulphites, is still far more than sufficient to enable free selenious acid to precipitate them from the nitrates. Mercuric selenite* is soluble in potassium selenite; so is mercuric oxide; and the solutions are not precipitable by potassium hydroxide. Further agreement fails. Mercurous selenite is not decomposed by potassium selenite into mercuric salt and mercury, and silver selenite does not dissolve in potassium selenite. This is somewhat remarkable, but is probably due to the affinities of selenium being so much weaker than those of sulphur and to silver forming less stable compounds than mercury with selenium, as well as with sulphur, silver sulphite being completely decomposed by mercury nitrates. The points of agreement, however, between selenites and sulphites leave but little doubt that the former, like the latter, have a hemihaloïd constitution.

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* The insoluble normal selenite. We have not succeeded in preparing Berzelius's soluble acid selenite.

But when silver selenite is treated with ethyl iodide, it yields dioxylic selenious ether, from which metallic selenites would appear also to be dioxylic, as Michaelis and Landmann have suggested they are, instead of being hemihaloïd like metallic sulphites. It cannot be admitted, however, that the iodide test is sufficient by itself to settle the constitution of an oxylic salt, for it gives conflicting testimony as to the constitution of nitrites. Only silver selenite yields the selenious ether; with potassium selenite it is difficult to get a reaction, and when this occurs, it leaves the selenium wholly deoxidised. Since ethylselenonic acid cannot be prepared by the oxidation method, it does seem allowable to suppose that in the reaction of the silver selenite a selenylic group changes into a selenosic one, so as to enter into oxylic union with the ethyl. To suppose this, is a way out of the difficulty certainly much easier than it would be to consider metallic selenites as dioxylic salts.

The Analogue of Sulphurous Acid among Carbon Compounds.

In the discussion of the paper by one of us on the constitution of some non-saturated oxygenous salts, Professor Tilden drew attention to the modification that might be needed in the present view of the constitution of carbonates, if that which was therein advocated for the sulphites should be adopted. The point then raised is a very interesting one, and has suggested to us a further ground for recognising the sulphonic constitution of sulphites, and also for regarding sulphur as only quadrivalent in sulphates as well as in these salts.

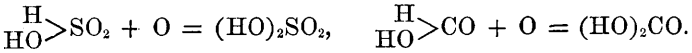
Beyond the fact that both sulphites and carbonates are easily decomposable salts, there is nothing specially to connect the two classes of salts. Indeed, even as regards their decomposability, the two classes could not be more unlike than they are in their mercury and silver members. Besides, carbonates are not oxidisable, whilst sulphites are readily oxidisable. It would, therefore, seem strange to require that a similar constitution should be found for the two classes of salts. Rather than this, there is surely a strong presumption that their constitution must be unlike. Nothing is more certain than that carbonates are dioxylic salts; nothing, therefore, would seem more likely than that sulphites should not be dioxylic.

Sulphites find their real analogue among carbon compounds, not in carbonates, but in *formates*, although differing from these in having the double atom of oxygen in their radicle, and in having the hydrogen, which in the acid is joined to the radicle, displaceable by metal.

Both sulphites and formates are monoxylic; both suffer oxidation to salts of dioxylic acids; and both suffer hydrolysis with similar effects when the basilous radicle is silver or mercury. The oxidisability of formates has always been remarkable, as contrasted with the high degree of stability of the acetates (and higher homologues), in presence of powerful oxidising agents. Now the difference in this respect between formates and acetates is due to the fact that the last remaining hydrogen-atom of methane (aldehydic hydrogen) is readily oxidisable, whilst methyl in place of it is not oxidisable. But this is precisely analogous to what was said in the former paper as to the reason why most metallic sulphites are oxidisable and organic sulphites are not. Methylsulphurous acid and acetic acid—

$$\begin{matrix}\mathrm{Me}\\\mathrm{HO}\end{matrix}\!>\!\mathrm{SO_2},\qquad \begin{matrix}\mathrm{Me}\\\mathrm{HO}\end{matrix}\!>\!\mathrm{CO},$$

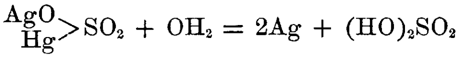
do not oxidise, whereas sulphurous acid and formic acid do oxidise.



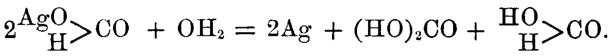
$$\begin{matrix}\mathrm{H}\\\mathrm{HO}\end{matrix}\!>\!\mathrm{SO_2} + \mathrm{O} = (\mathrm{HO})_2\mathrm{SO_2},\qquad \begin{matrix}\mathrm{H}\\\mathrm{HO}\end{matrix}\!>\!\mathrm{CO} + \mathrm{O} = (\mathrm{HO})_2\mathrm{CO}.$$

In this oxidation, the carbon does not change in valency; therefore, there is no reason to consider the sulphur as doing so. There is good evidence of sulphur being quadrivalent in sulphites, and therefore also in sulphates. If the sulphur is quadrivalent, the oxygen of sulphuryl forms a bivalent double atom; and that it does so is rendered still more probable by its apparent solidarity in the changes which the sulphuryl may undergo,* and by sulphuryl functioning so very like carbonyl.

The hydrolysis of silver sulphite affects, of course, the whole salt, because its acid is bibasic though monoxylic, whilst the hydrolysis of silver formate affects only half the salt; in both cases, metal is replaced by the hydrogen of the water:—



$$\begin{matrix}\mathrm{AgO}\\\mathrm{Hg}\end{matrix}\!>\!\mathrm{SO_2} + \mathrm{OH_2} = 2\mathrm{Ag} + (\mathrm{HO})_2\mathrm{SO_2}$$



$$2\begin{matrix}\mathrm{AgO}\\\mathrm{H}\end{matrix}\!>\!\mathrm{CO} + \mathrm{OH_2} = 2\mathrm{Ag} + (\mathrm{HO})_2\mathrm{CO} + \begin{matrix}\mathrm{HO}\\\mathrm{H}\end{matrix}\!>\!\mathrm{CO}.$$

Sulphurous acid and formic acid both readily convert mercuric chloride to mercurous chloride. Sodium sulphite and sodium formate are both producible by the action of sodium hydroxide on the respective acid oxides—SO_2 and CO.

Formic acid being the analogue of sulphurous acid, carbonic acid represents sulphuric acid; carboxylic acids sulphonic acids (a relation which has long been recognised); and oxalic acid, hyposulphuric

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* If thionyl chloride and silver nitrate do really produce in the first instance nitrosyl chlorosulphonate, as, according to Thorpe, they appear to do (Trans., 1882, 297), an exception after all exists to the statement that oxidation to sulphuryl does not occur in two stages (see Trans., 1885, 215).

acid. Hyposulphuric acid by hydrolysis becomes sulphurous and sulphuric acids; oxalic acid by the same kind of change becomes formic and carbonic acids. The analogy is complete, and surely it must be the case, therefore, that sulphites are only monoxylic salts.

Action of Phosphorus Oxychloride on Sulphites.

In a note to the paper on this subject (Trans., 1885, 207) one of us expressed a doubt as to whether Carius had ever tried, as he was said to have done, the action of phosphorus oxychloride on sulphites. This was done because the results of our own experiments differed apparently from those given on his authority, and because the reference in *Watts's Dictionary* to his paper was found to be wrong. In consequence of the expression of this doubt, Professor Schorlemmer, at a subsequent meeting of the Society, gave the correct reference to Carius's memoir, *Annalen*, **106**, 330, and also some account of what Carius had observed. The back volumes of the *Annalen* have since fortunately come within our reach,* and we have now seen Carius's own words.

The first point important to notice is that he calls attention to the difficulty of getting any sulphite quite dry without decomposition; he succeeded only with the calcium salt, and even that had to be kept in a current of dry air for a long time at 150°. This confirms the surmise contained in the former paper that, in our experiments the sulphites, well-dried as they were supposed to be, must have retained some moisture; only slight action was observed, even when the phosphorus oxychloride was repeatedly distilled off from the sulphite and run back upon it. It was therefore stated that "it is probable that thoroughly dry and pure sulphites are not acted on at all by pure phosphorus oxychloride;" this is just the result of Carius's more accurate experiments. Calcium sulphite is not acted on at all by phosphorus oxychloride at common temperatures, nor even, except to a very slight extent, when the temperature is maintained for some time at 120° under pressure; but it is acted on freely at 150°.

The nature of this action is the second important point in connection with the constitution of sulphites. To make thionyl chloride—for that was his purpose, and not the investigation of the constitution of sulphites—Carius first took 2 mols. of phosphorus oxychloride to 3 mols. of calcium sulphite, in accordance with the equation—

$$3CaSO_3 + 2POCl_3 = Ca_3(PO_4)_2 + 3SOCl_2.$$

Proceeding in this way he failed, not however for want of a reaction at 150°, but because he got large quantities of sulphur dioxide (which

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* A set has lately been added to the library of the Imperial University of Japan.

burst his sealed tubes). An equation such as was used in the former paper might serve to express this generation of sulphur dioxide:—

$$6CaSO_3 + 2POCl_3 = Ca_3(PO_4)_2 + 3CaCl_2 + 6SO_2,$$

and, so far, nothing is seen to support the view that sulphites are thionyl compounds—dioxylic salts. As a test of their chemical constitution the reaction has clearly failed, if it does not, indeed, favour their having a sulphonic constitution.

But *some* thionyl chloride is also formed, which makes the matter much less simple; and, besides, half only of the phosphorus oxychloride taken is accounted for in the equation just set down. How material the rest of the oxychloride is to the production of the thionyl chloride, appears from the effects of using a greater proportion of oxychloride in the experiment. Carius found, after repeated trials, that by raising the proportion of oxychloride until equal molecular proportions of the two substances were present, the proportion of thionyl chloride greatly increased, and that of sulphur dioxide became very small. Calcium sulphite can thus be made to yield most of its sulphur as thionyl chloride, but only by using excess of phosphorus oxychloride, since without this excess sulphur dioxide is the main product. Now, this sulphur dioxide must be derived from thionyl chloride should phosphorus oxychloride really act on calcium sulphite, and then form thionyl chloride by this action.

For this, however, to be the true explanation of the production of the sulphur dioxide, some of the sulphite and the oxychloride should remain without acting on each other; because in one case the presence of the phosphorus oxychloride must be supposed to preserve in some way the thionyl chloride from conversion into sulphur dioxide, or in the other case some calcium sulphite must react with the thionyl chloride so as to generate sulphur dioxide:—

$$CaSO_3 + SOCl_2 = CaCl_2 + 2SO_2.$$

This is by no means an impossible reaction, but it is as yet unknown to occur, while its doing so here would depend, as above stated, on the improbable condition that the calcium sulphite to take part in it is to be had as wanted even in presence of phosphorus oxychloride, which for some reason has become inactive on it. This, indeed, seems to remove all chance of its being what actually happens; for just in the case where the phosphorus oxychloride is used in abundance, there is thionyl chloride got in abundance, and nearly without sulphur dioxide. The other view of the matter, that phosphorus oxychloride may in some way preserve the thionyl chloride from decomposition, does not need examining. If this is agreed to, then there is nothing to be said for the view that thionyl chloride is the source of the sulphur dioxide.

Taking into account these three points concerning the production of thionyl chloride from a sulphite—that a high temperature is necessary; that an excess of phosphorus oxychloride must be present; and that sulphur dioxide is the principal and primary product when no more than the normal quantity of the reagent is used—it cannot be allowed that the thionyl chloride is the direct product of a reaction between the sulphite and the oxychloride. It is not difficult to find another origin for it.

Gustavson has shown that when phosphorus oxychloride is heated at the temperature Carius employed, 150°, along with boron oxide, not only is some of the boron oxide converted into chloride, but phosphorus pentoxide is produced and unites with unchanged boron oxide. What takes place when it is heated at 150° with calcium sulphite appears, then, to be this: in its own form it remains without action on the sulphite; it behaves potentially as, or else it gradually dissociates into, phosphorus pentoxide and pentachloride; the pentoxide takes calcium oxide from the sulphite, thus setting free sulphur dioxide; and this with the phosphorus pentachloride gives thionyl chloride and phosphorus oxychloride again (Schiff's reaction). The following equations serve to express these reactions:—

$$10POCl_3 = 2P_2O_5 + 6PCl_5,$$
$$6CaSO_3 + 2P_2O_5 = 2Ca_3(PO_4)_2 + 6SO_2,$$
$$6SO_2 + 6PCl_5 = 6SOCl_2 + 6POCl_3.$$

Three-fifths of the phosphorus oxychloride begun with are thus regained. In practice, Carius found an extra half of the oxychloride to be excess enough to use, which is quite intelligible, since the excess can serve over and over again. The large quantity of sulphur dioxide which forms when these proportions are greatly altered in favour of the calcium sulphite, is to be traced to the action of the phosphorus pentachloride upon the excess of calcium sulphite instead of upon the sulphur dioxide, as is shown by the following equation, intended to take the place of the last one in the scheme of reactions just formulated, on the supposition that 15 mols. of calcium sulphite are present in addition to the 6 mols. there set down:—

$$15CaSO_3 + 6PCl_5 = 3Ca_3(PO_4)_2 + 6CaCl_2 + 9SOCl_2 + 6SO_2.$$

With the other $6SO_2$ liberated, but now not decomposed, there are thus obtained $12SO_2$ to $9SOCl_2$. The calcium chloride here shown is a necessary complement to the sulphur dioxide, whatever version of the change be adopted.

In spite, then, of the production of thionyl chloride when sulphites are strongly heated with phosphorus oxychloride, it still remains true that the changes observed *afford no support* to the view that those salts are dioxylic and decomposable according to the equation—

$$3CaSO_3 + 2POCl_3 = (CaO_2)_3(PO)_2 + 3SOCl_2.$$