JOURNAL OF THE COLLEGE OF SCIENCE, IMPERIAL UNIVERSITY,
TŌKYŌ, JAPAN.
VOL. XIX., ARTICLE 15.

Peroxylaminesulphonates and Hydroxylaminetrisulphonates (Sulphazilates and Metasulphazilates, Fremy).

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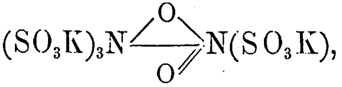
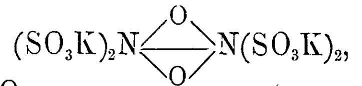
Perhaps the most interesting of the sulphazotised salts discovered by Fremy (*Ann. Chim. Phys.*, 1845, iii, **15**, 408) are the two which result from the oxidation of one or other of the potassium hydroximinosulphates (hydroxylaminedisulphonates) in aqueous solution by either silver oxide or lead peroxide or some other reagent. One of these products is the very unstable salt which he named *sulphazilate.* It is remarkable for crystallising from its aqueous solution, which is of an intense bluish-violet colour, in brilliant golden-yellow needles, very slightly soluble in ice cold water, but easily dissolving in hot water. It can seldom be long preserved and gives a disagreeable odour to the skin, like that caused by manganates and ferrates. According to Fremy, it is easily fusible, but that is a mistake; it is the products of its decomposition which melt. The other salt, his *metasulphazilate*, is also sparingly soluble in cold water, but is colourless and has considerable stability. It crystallises in rhombic prisms which are so well defined that Fremy describes the compound as being the most beautiful of all the sulphazotised salts. These crystals appear to be isomorphous with those of 5/6–normal potassium hydroximinosulphate, and the two salts can hardly be separated by crystallisation. Its solution is quite neutral and gives a precipitate with basic lead acetate only. Fremy expressed the composition of the sulphazilate by the formula, $HO_7NS_2K_2$ (here written with the atomic proportions now in use), which is only incorrect in including hydrogen (Claus). He gave the composition of the metasulphazilate correctly as $H_6O_{23}N_2S_6K_6$.

Claus (*Annalen*, 1871, **158**, 205) who gave details for the preparation of the coloured salt by lead peroxide, proved that in its production from 5/6-normal potassium hydroximinosulphate it is not necessarily accompanied by sulphate; he also demonstrated with tolerable certainty that it is the sole product of the oxidation; and found that it passed spontaneously into the colourless salt, together with a fixed quantity of sulphate and a gas which is apparently nitrous oxide (compare page 16 of this paper). He recognised the sulphonate constitution of both salts and gave to the coloured salt the name and formula, 'oxysulphazotate,'  $(SO_3K)_3N{<}\overset{O}{\underset{O}{\longrightarrow}}{>}N(SO_3K)$, and to the white salt the name and formula, 'trisulphoxyazoate,' $O{:}N(SO_3K)_3$, H_2O, that is, with the nitrogen quinquevalent in both formulæ. It will be seen that, even empirically these formulæ differ a little from Fremy's. Claus also sought for, and, as he believed, obtained the primordial sulphazotised salt, which he formulated at first as SO_2,NO_2K (*op. cit.*, 213), and afterwards as $O{:}N(SO_3K)$ (*Ber.*, 1871, **4**, 508). This would be the analogue of the 'trisulphoxyazoate,' only with the nitrogen trivalent; but the existence of this salt has since been disproved (this Journ., 1900, **13**, 219).

Raschig (*Annalen*, 1887, **241**, 223) having found that the white salt, in a boiling and feebly acid solution, may yield sulphate to the extent of two-thirds of its sulphur, along with, apparently, hydroxyaminosulphuric (hydroxylaminemonosulphonic) acid, has recognised that it behaves as a derivative of hydroxylamine. But, because it does not decompose when in strongly alkaline solution, he will not allow that it is that base trisulphonated. He modifies Claus's two formulæ, writing that for the coloured salt as  $(SO_3K)_2N\overset{O}{\underset{O}{\diamond}}N(SO_3K)_2$, and that for the white salt as  $(SO_3K)_3N<\substack{O\\O}>N(SO_3K)_3$, $2H_2O$.

Hantzsch and Semple have found (*Ber.*, 1895, **28**, 2744), that, when crystals of 2/3-normal potassium hydroximinosulphate form in a bluish-violet solution of potassium sulphazilate, they may contain 1–4 percent. of this salt, apparently in solid solution, and consequently show bluish-violet colour. These chemists have therefore advanced the view that Fremy's coloured salt, which they have re-named 'nitroxydisulphonate,' is sulphonated nitric peroxide, the orange-yellow crystals of which have double the molecular magnitude of its dissolved bluish-violet form, in analogy with the two forms of nitric peroxide itself. The formula for the bluish-violet modification is given in a foot-note as $O\cdot N:(SO_3K)_2$, in which, therefore, the nitrogen is represented as being trivalent and the oxygen as univalent. A structural formula for the yellow modification is not given, but Raschig's is rejected, as having two quinquevalent nitrogen atoms in union with each other, a mode of combination which is without parallel. Raschig's formula for the white salt is also rejected, but as the simpler one proposed by Claus is adopted in its place, the quinquevalency of the nitrogen is maintained. On the authority of Schatzman, and as a result of their own experiments in the case of hydriodic acid, these chemists state that, in acting as an oxidising agent, the coloured salt reverts to hydroximinosulphate.

In 1896, Sabatier (*Compt. rend.*, **122**, 1417, 1479, and 1537; **123**, 255) published the results of an investigation of the violet solutions produced by reducing agents acting on a sulphuric acid solution of nitrososulphuric acid, and suggested that the colour is due to the formation of the acid of Fremy's potassium sulphazilate. His suggestion is discussed on page 22 of this paper.

In the detailed examination of Fremy's sulphazotised salts made by Dr. Divers and the author, the results of which have been described from time to time in this Journal, the sulphazilate and metasulphazilate were purposely reserved for separate treatment, because they are distinguished from the other salts in being products of oxidation. In the present paper the author endeavours to prove (1) that the sulphazilate is an *oxime-peroxide* (*Scholl*) or a *peroxime*, $(SO_3K)_2NO{\cdot}ON(SO_3K)_2$, the first and only inorganic peroxime yet known; (2) that the metasulphazilate is a *triacylated hydroxylamine*, $(SO_3K)_2NO(SO_3K)$, the only compound of this type having an established normal constitution (all others, such as tribenzhydroxylamine, being apparently of more complex constitution); and (3) that, consequently the nitrogen, in both these sulphazotised salts is only trivalent, instead of being quinquevalent.

From among the several constitutional names which suggest themselves for Fremy's provisional 'sulphazilate' and 'metasulphazilate,' that of *peroxylaminesulphonate* for the former, and of *hydroxylaminetrisulphonate* for the latter, have been adopted as preferable. In consequence, it has been found advantageous in this connection to call the parent salt *hydroxylaminedisulphonate* instead of the alternative *hydroximinosulphate*, the name usually employed by Divers and the author. It has also been found to be convenient to treat of the hydroxylaminetrisulphonates before the peroxylaminesulphonates, from which they are apparently always derived.

Hydroxylaminetrisulphonates
(*Metasulphazilates*; *Trisulphoxyazoates*).

Potassium hydroxylaminetrisulphonate is most readily prepared by Fremy's method, in which no intermediate separation is made of its parent salt, the peroxylaminesulphonate. Somewhat alkaline potassium hydroxylaminedisulphonate is gently boiled and shaken with silver oxide or lead peroxide, until the solution, which at first becomes intensely bluish-violet, just loses its colour. Then, by evaporation and cooling, the filtered solution can be made to yield nearly all its hydroxylaminetrisulphonate. Theoretically, all the hydroxylaminedisulphonate should be converted into hydroxylaminetrisulphonate and nitrite,

$$2PbO_2+3HON(SO_3K)_2+KOH=2Pb(OH)_2+2ON(SO_3K)_3+KNO_2;$$

but sulphate and nitrous oxide are always produced, usually accompanied by very small quantities of nitrogen and aminemonosulphonate (aminosulphate). Nevertheless, 86 and 87.8 per cent. yields of the indicated quantity of the salt have been obtained, together with 78 and 85 per cent. of the full amount of nitrite as indicated by the urea method (p. 24). The production of such large quantities of the hydroxylaminetrisulphonate shows the inaccuracy of Claus's description of the changes concerned. According to that account, which is endorsed by Raschig, no nitrite is formed and the utmost yield of hydroxylaminetrisulphonate would be equivalent to only 75 per cent. of the sulphur of the hydroxylaminedisulphonate.

Constitution.—Strictly speaking, the product of the triacylation of hydroxylamine with sulphonate radicals can only be a disulphonate, the third sulphonate radical becoming sulphatic by its union with oxygen. But the name of hydroxylaminetrisulphonate is sufficiently appropriate for such a compound, since, although a sulphatic salt, it is not actually a sulphate, but a mixed anhydride of acid salts, one being the 2/3-normal hydroxylaminedisulphonate and the other the acid sulphate:

$$(SO_3K)OH+HON(SO_3K)_2=H_2O+(SO_3K)\cdot O\cdot N(SO_3K)_2.$$

Lossen (*Ber.*, 1892, **25**, 440) has already pointed out that dibenhydroxamic acid may be regarded as the mixed anhydride of benzhydroxamic acid and benzoic acid, and similarly in the case of other diacylhydroxylamines.* Nitrososulphuric acid (nitrosyl hydrogen sulphate), the mixed anhydride of nitrous and sulphuric acids, is an example of a mixed inorganic anhydride. But the present salt, as the anhydride of two different acid salts, finds its close analogue in potassium hyponitrososulphate, $(SO_3K)O(N_2OK)$ (Pelouze's 'nitrosulphate,' Journ. Chem. Soc., Trans., 1885, **47**, 203, this Journal, **9**, 101, 277) which is the anhydride of acid hyponitrite and acid sulphate. The two mixed anhydrides agree in being stable in alkaline solution and unstable in acid solution, and in not giving barium sulphate with barium hydroxide or chloride.

The evidence that the metasulphazilates have the constitution of hydroxylaminetrisulphonates is simple and direct, and similar to that as to the constitution of the hyponitrososulphates. In the first place, sodium amalgam decomposes them, apparently quantitatively (p. 26), into sulphate and normal aminedisulphonate (iminosulphate):—

$$KO{\cdot}SO_2{\cdot}O{\cdot}N(SO_3K)_2+2Na=KO{\cdot}SO_2{\cdot}ONa+NaN(SO_3K)_2,$$

no sulphite being formed. Instead of sodium amalgam, the zinc-copper couple may be used with the boiling solution to reduce hydroxylaminetrisulphonates (p. 28), but in this case the aminedisulphonate is apt to hydrolyse during the heating. The result of this reduction of the salts not only proves their sulphatic constitution but shows also that neither the formula, $ON(SO_3K)_2$ (Claus, Hantzsch), nor this formula doubled (Raschig) can possibly be right, because its

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* Twenty-six years ago, Koenigs (*Ber.*, 1878, **11**, 615 and 1588) found that benzenesulphinic and nitrous acids react to form hydroxylaminedibenzsulphinic (dibenzsulphydroxamic) acid, and that this with more nitrous acid becomes a tribenzsulphinic compound. Preliminary experiments made for the author seem to show that the latter will almost certainly prove to be hydroxylaminetribenzsulphinic acid. Its production may probable be expressed by the following equation:—

$$6C_6H_5SO_2H+4HONO=2(C_6H_5SO_2)_2N{\cdot}O(SO_2C_6H_5)+N_2O+5H_2O.$$

acceptance would require that the sodium should act as a 'carrier' of oxygen to the sulphonate radical. Dunstan and Goulding (*Journ. Chem. Soc.* Trans., 1899, **75**, 792) have found that trialkyloxamines, *e.g.*, $(CH_3)_3N:O$, are reduced to trialkylamines by zinc and acid. Were metasulphazilates also oxaminic in constitution, they too should be reduced to aminetrisulphonates (nitrilosulphates). Sulphites, and even sulphur dioxide have no action on the hydroxylaminetrisulphonates (p. 29).

In the second place, the metasulphazilates behave as sulphonated hydroxylamine. They reduce acidified permanganate; they give up one-third of their nitrogen in the form of ammonia when they are heated with soda-lime (Claus); and they can be hydrolysed ultimately into hydroxylamine and acid sulphate. Although very stable salts in other respects, they cannot, indeed, remain in solution very long or be kept for many months in the solid state without beginning to hydrolyse. But if a small amount of potassium or sodium hydroxide or, much more conveniently, of ammonia is added to their solution, they are permanent even for years in closed vessels. The other and less sulphonated hydroxylamines have no such stability, but always revert more or less to sulphite and either nitrite or nitrous oxide. The hydrolysis is expressed by the equation :

$$(SO_3K)ON(SO_3K)_2+3H_2O=3H_2SO_4+HONH_2.$$

Taking into consideration their water of crystallisation, the potassium and the ammonium hydroxylaminetrisulphonates can only be written with doubled formulæ, thus in some degree supporting Raschig's action in doubling Claus's formula for the former salt. But a cryoscopic measurement (p. 33) of the molecular magnitude of the sodium salt has shown that the simple formula is correct.

Potassium Hydroxylaminetrisulphonate, $2(SO_3K)ON(SO_3K)_2, 3H_2O$, hitherto the only known salt, occurs in flattened monosymmetric prisms, measurements of which have been made by Fock (Raschig).

Its solubility in water at 18° is one in 25.37 parts. It is neutral to phenolphthalein, litmus, methyl-orange, and other indicators. When slowly heated to 100-120° in the air, it loses some of its water of crystallisation and is then hydrolysed by the remainder, acting together with the moisture of the atmosphere, so that at first it loses in weight and then gains. The residual mass is strongly acid owing to the presence of acid sulphate. It has not been found possible to avoid hydrolysis, even when the salt is very gradually heated in a current of dried air, after having already been exposed in a desiccator at the ordinary temperature. Its water, therefore, could only be determined by difference. As expressed in the foregoing formula, which agrees with Fremy's empirical formula, it is certainly 3/2 H_2O; although Claus made it out to be 1/1 H_2O only. In his paper, five concordant analyses of the anhydrous salt, besides four analyses of the hydrated salt, are given; and so far from reference being made to any difficulty being experienced in rendering the salt anhydrous, it is stated that the water of crystallisation easily escapes at 100°. But it is important to note that his four determinations of the water give numbers which are all somewhat higher than those required by his calculation, although the salt occurs in large, clear, non-deliquescent crystals, and that the figures thus calculated are but little if any higher than those obtained by the author in two direct determinations of loss of water by heating, in which the residues were always acid and therefore contained water. The salt has also been analysed by Raschig, but his results are not decisive one way or the other (p. 30).

Sodium Hydroxylaminetrisulphonate, $(SO_3Na)ON(SO_3Na)_2, 2H_2O$.— This salt, now prepared for the first time, is obtained by boiling a solution of 2/3-normal sodium hydroxylaminedisulphonate and its equivalent half-molecule of sodium hydroxide with lead peroxide. It is more difficult to purify from accompanying salts than the potassium salt, but by very cautious addition of sulphuric acid, these salts may be converted into sulphate, which can be easily separated from the hydroxylaminetrisulphonate by freezing. It crystallises in aggregates of small, tabular, monoclinic crystals (p. 31). The solubility of the salt is considerable, one part requiring only 2.83–2.85 parts of water at 21.5°. Like the potassium salt, it is neutral to indicators, and, when heated, hydrolyses in its water of crystallisation.

Ammonium Hydroxylaminetrisulphonate, $H_{30}O_{23}N_8S_6$ or

$$2(SO_3NH_4)ON(SO_3NH_4)_2,3H_2O.$$

The analysis of this salt confirms the view that the amount of water present in the potassium salt is greater than that found by Claus. The ammonium salt forms thick, rhombic plates and prisms, similar to those of the potassium salt and probably isomorphous with them. But goniometric examination was impracticable, for although some faces were 7–9 mm. long, others were too imperfectly developed for determination. The salt is neutral to litmus and methyl-orange, and generally like the potassium salt, but it is exceedingly soluble in water, one part dissolving in 0.61 part at 16°. The salt examined was prepared by digesting the basic lead salt with ammonium carbonate and evaporating the solution on the water-bath until it had almost lost its alkalinity, and then concentrating it further under reduced pressure over solid potassium hydroxide. Its nitrogen and sulphur were found to be in much closer agreement with the formula showing 3/2 molecules of water; but here again the difference between the numbers for the two formulæ is not very great (p. 32).

Hydroxy-lead Hydroxylaminetrisulphonate, $H_9O_{19}NS_3Pb_6$ or

$$ON(SO_3PbO{\cdot}PbOH)_3,3H_2O.$$

This tetrabasic and very insoluble lead salt, which appears to be the only insoluble hydroxylaminetrisulphonate, was prepared by pouring a warm solution of the potassium salt into excess of carefully prepared basic lead acetate solution. It is a chalky powder readily decomposed by a solution of an alkali carbonate (p. 32).

Peroxylaminesulphonates
(*sulphazilates ; oxysulphazotates ; nitroxydisulphonates*).

Only silver oxide and lead peroxide have, as yet, been used in the preparation of a peroxylaminesulphonate, but many other oxidising agents produce the violet coloration, thus indicating the conversion of a hydroxylaminedisulphonate into peroxylaminesulphonate, as was pointed out by Fremy ; even chlorine when used in limited quantity is able to produce this change. Ozone is an excellent reagent, rapidly producing a strong solution of the peroxylaminesulphonate when it is passed into a faintly alkaline solution of the hydroxylaminedisulphonate. Nitrous fumes are absorbed by an ice-cold solution of this salt, which assumes a dark brown colour, and this solution, when rendered alkaline slowly acquires the violet colour of the peroxylaminesulphonate. Also, when an ice-cold solution of potassium hydroxylaminedisulphonate and nitrite is barely acidified, preferably with sulphur dioxide, similar effects are produced. The temporary production of a violet colour is frequently observed in experiments made with the compounds of potassium nitrite with potassium hydroxylaminedisulphonates (this Journ. **13**, 211). Hydrogen peroxide, potassium ferricyanide, potassium permanganate, and alkaline cupric solutions are all inactive with it. Even freshly precipitated mercuric oxide is without action upon it, although it is more quickly affected by light when it is suspended in a solution of the salt.

In preparing potassium peroxylaminesulphonate, Fremy showed a preference for the use of silver oxide, whilst Claus, who assumed that the action of silver oxide was apt to proceed too far, preferred lead peroxide. Silver oxide gives a somewhat better yield and none of the silver goes into solution, whereas a little of the reduced lead peroxide dissolves and renders the salt impure. But the dissolved lead is readily removed and the lead peroxide presents the advantage of being at hand when wanted, whilst the silver oxide has to be prepared each time and the metal afterwards recovered. Lead peroxide has therefore been used in the present research.

Fremy used either the 2/3- or the 5/6-normal potassium hydroxylaminedisulphonate as the source of the peroxylaminesulphonate; Claus used only the latter, and Raschig chose the former. The advantage lies with the 5/6-normal salt, for, when prepared from a less alkaline salt, the peroxylaminesulphonate proves to be less easily purified and consequently less stable. The 5/6-normal salt is always so far hydrolysed in dissolving that it is converted into the 2/3-normal salt, the potassium hydroxide being left in solution as noticed by Claus. The presence of free alkali, however, moderates the action of the oxidising agent, and to such an extent that a sufficiently concentrated solution of the very soluble normal sodium hydroxylaminedisulphonate is not attacked at all by lead peroxide. Apparently, therefore, lead peroxide acts as an acid oxidiser, in the form of plumbic anhydride, as suggested by Fremy.

The salt, which must be prepared just when it is wanted, is produced by mixing about 6 grams of the 5/6-normal hydroxylaminedisulphonate (or the same amount of the 2/3-normal salt together with a small quantity of a potassium hydroxide) and a little more than the same weight of lead peroxide (or of the silver oxide precipitated from a little less than the same weight of silver nitrate) and making up with water to 25 c.c. The mixture is agitated for 15 minutes in water near to, but not above, 40°. Then, the solution is decanted without delay, treated with carbon dioxide (when lead peroxide has been used), and filtered, before crystallisation sets in. The solution should therefore be kept warm up to this point. When it has remained some hours in an ice-box, almost the whole of the peroxylaminesulphonate will have separated as a crust of minute orange yellow needles. These can be recrystallised, but not without material loss from hot water made slightly alkaline with potassium hydroxide. When, as appears to have been the case with Fremy, much hydroxylaminedisulphonate has been left unoxidised, some of this will be found with the peroxylaminesulphonate, from which it can hardly be wholly separated by recrystallisation, its crystals remaining coloured by the peroxylaminesulphonate, as observed by Hantzsch and Semple.

Any close determination of the yield cannot be made directly, since the salt can rarely even be roughly weighed before decomposition sets in. Its amount has, therefore, to be estimated by letting it decompose, igniting the residue with ammonium carbonate, and weighing the potassium sulphate. In this way the yield of separated salt was found to be a very little over three-fourths of the calculated quantity, when silver oxide was used ; and a little less than two-thirds when lead peroxide was taken. But by indirect means, the amount of the salt actually produced can be shown to be much higher than this. As already mentioned (p. 5), the exhaustive oxidation by lead peroxide of a hot solution of hydroxylaminedisulphonate has given nearly 88 per cent. of the calculated quantity of hydroxylaminetrisulphonate, a fact which signifies that at least as much peroxylaminesulphonate as is equivalent to this percentage of the total sulphur must have been formed, since its production is intermediate to that of the hydroxylaminetrisulphonate.

Potassium peroxylaminesulphonate is very unstable in water and very little soluble in the cold. In N/10-solution of potassium hydroxide, which fairly represents its usual mother liquor, it is more stable, but still less soluble; 100 parts at 3° dissolve only 0.62 part of the salt, and at 29° only 6.6 parts (p. 33). It interacts in solution with normal potassium sulphite and then produces hydroxylaminetrisulphonate and hydroxylaminedisulphonate, evidently in molecular proportions (p. 34), this change being a fact of great theoretical importance. Its chemical activity is manifested in oxidising certain easily oxidisable substances and being thereby reduced to its parent salt, hydroxylaminedisulphonate. Although it liberates iodine from hydriodic acid, it fails to oxidise hydrochloric acid. When the latter acid in concentrated solution is poured upon the solid salt, it sets up the same decomposition as that which occurs spontaneously (p.15). But here, as the rise of temperature is moderated, definite although minute quantities of aminemonosulphonate and of hydroxylamine (not its sulphonate) can be found. The salt has practically no action on alcohol ; nitrous and sulphurous acids rapidly reduce it, so also does sodium amalgam, first to hydroxylaminedisulphonate (as already observed by Schatzman), and then this salt passes slowly but completely into aminedisulphonate (iminosulphate). Clean granulated zinc slowly reduces the salt, but copper does not. The spontaneous decomposition of the salt may, however, easily be mistaken for its slow reduction by a reducing agent, since in this case also, as will be presently described (p. 16), hydroxylaminedisulphonate is produced. The difference is readily detected by testing for nitrite, which is produced only in the spontaneous decomposition of the salt. Manganese dioxide very slowly decomposes it, causing a minute effervescence ; lead peroxide is inactive. Potassium permanganate is reduced to green manganate. Clean filter-paper, unlike the paper in use in Fremy's time, does not affect it.

Part of the instability of peroxylaminesulphonates must be attributed to the presence of oxidisable impurities. Thus, Fremy noticed the decomposing action of atmospheric dust; whilst nitrite, another impurity liable to be found in the salt, also greatly increases its instability. Acids hasten the decomposition of the salt; alkalies retard it. When drained on the tile from an alkaline solution, the salt may, under cover, remain undecomposed for two hours or more ; but if washed on the tile and thus deprived of the traces of its adherent alkaline mother liquor, it will decompose in a very few minutes. Nevertheless, on one occasion, some of the salt thus purified was kept on a tile for 11 months in a desiccator, and only then decomposed through an accident. This, however, must be regarded as a very uncommon experience. The sensitiveness of potassium peroxylaminesulphonate to acids has been recorded by others, but has been somewhat exaggerated. When the salt is free from every trace of nitrite, its cold acidified solution may remain coloured for 40 minutes. An alkaline solution may not lose all its colour when kept in a closed vessel for more than a month. If sufficiently pure, the solid salt may be preserved for a day or so under water rendered slightly alkaline with potassium hydroxide.

The nature of the decomposition of potassium peroxylaminesulphonate occurring in the absence of alkali has already been examined, although in all cases very imperfectly, by Fremy and by Claus, and in the presence of alkali by Raschig. According to Fremy, the solid salt decomposes explosively when heated ; when exposed to the air it becomes strongly acid ; and when heated in solution it yields sulphate and a gas mistaken by him for oxygen, but which is really nitrous oxide. He was also mistaken in stating that it melts readily and that when left in a closed bottle it evolves nitric oxide. Claus found that, whether in the solid state or in solution, whether when cold or moderately heated, the decomposing salt yields hydroxylaminetrisulphonate and nitrous oxide, together with acid sulphate equivalent to one-fourth of its sulphur, according to the equation $2K_4N_2S_4O_{14}+H_2O=2KHSO_4+2K_3NS_3O_{10}+N_2O$. Raschig has confirmed Claus's statements and also states that the solid salt or its solution, also decomposes in this way even when left in contact with alkali. He also adds that its solution when acidified is decolorised in a few minutes, whilst in presence of alkali it can in some cases be heated to boiling without change. All these statements by Claus and Raschig require to be modified in order that they may accurately describe the behaviour of the salt, and even then they fail to indicate the primary change which the decomposing salt undergoes. Thus, the acid sulphate produced is seldom equal to one-fourth of the total sulphur, although it may be so, as twice found by Claus, and indeed also in the present investigation, but only when the salt had been used with too small a quantity of water to dissolve it all on warming. Owing to this fact, only a part of the nitrogen, which does not become hydroxylaminetrisulphonate, appears as nitrous oxide, along with a small amount of free nitrogen.

Solid potassium peroxylaminesulphonate is too unstable when dry and free from alkali, to exist many minutes without rapidly and almost explosively decomposing. In this decomposition, slight white fumes of ammonium salt (probably pyrosulphite and pyrosulphate), nitrogen and nitrous oxide, and a small quantity of sulphur dioxide are given off, whilst the residue, when the mass of the salt has been at all considerable, gets very hot (above 300°?) and melts. This residue consists of potassium sulphate (principally pyrosulphate) with a very little ammonium salt. Sometimes a trace of aminemonosulphonate can be detected by the mercuric nitrate test; also a trace of hydroxylamine (or other substance reducing alkaline cupric solution), but none of the other sulphonates, the temperature having been too high to leave these substances undecomposed.

The true products of the spontaneous decomposition of a peroxylaminesulphonate are only found (in company with small quantities of apparently secondary products) when the salt is heated to boiling with enough water to dissolve it, and in presence of sufficient alkali to prevent both the acidification of the solution during the decomposition of the salt and also the secondary changes which would result from acidification. The alkali does not appear to modify the nature of the primary change, although it distinctly increases the stability of the salt, as already mentioned (p. 14). When carried out in the foregoing manner, the decomposition of a peroxylaminesulphonate proceeds largely in such a way that not only do three-fourths of the sulphur of the salt, as suggested by Claus and by Raschig, together with one-half of its nitrogen, come out as hydroxylaminetrisulphonate, but the rest of the sulphur and one-fourth of the nitrogen become hydroxylaminedisulphonate again, whilst the remaining one-fourth of the nitrogen appears as nitrite,

$$2(SO_3K)_4N_2O_2+H_2O=2(SO_3K)_3NO+(SO_3K)_2NOH+NO_2H,$$

although some nitrous oxide and sulphate, besides minute and uncertain quantities of other substances, are always produced (p. 20)

This result explains the production of the large quantities of acid sulphate and nitrous oxide observed by Claus and Raschig, for the nitrous acid when not neutralised by alkali interacts with the hydroxylaminedisulphonate and yields acid sulphate and nitrous oxide (this Journ., **13**, 212.)

The generation of hydroxylaminedisulphonate in the spontaneous decomposition of a peroxylaminesulphonate accounts for the fact, met with in the present investigation, that much more hydroxylaminetrisulphonate is obtainable by heating hydroxylaminedisulphonate in solution with excess of lead peroxide than can be derived from the decomposition (out of contact with lead peroxide) of the peroxylaminesulphonate equivalent to that quantity of hydroxylaminedisulphonate (p. 5). For in presence of lead peroxide, that hydroxylaminedisulphonate which is regenerated by the independent decomposition of the peroxylaminesulphonate is oxidised again to more of this salt, to be again decomposed in the same way, until the whole of the disulphonate has become trisulphonate and nitrite, except that part of it which is lost as sulphate and nitrous oxide. Remembering that $4(SO_3K)_2NOH$ gives $2(SO_3K)_4N_2O_2$, the larger yield of hydroxylaminetrisulphonate which should result will be seen, on comparing the equation on page 5 with that just given, to be theoretically as 4 to 3. It will now, too, be evident, on reference to Claus's memoir, that his incomplete knowledge of the nature of the decomposition of the peroxylaminesulphonate led him to object too much to Fremy's account of the action of the oxidising agent in producing hydroxylaminetrisulphonate.

Constitution.—The constitution of a peroxylaminesulphonate as a sulphonate was recognised by Claus, and is deducible from the fact that it is formed by the dehydrogenation of hydroxylaminedisulphonate. The problem of its constitution as a nitroxy-compound remains to be solved, and the description just given of the potassium salt amounts to a demonstration, first, that its constitution is that of a peroxide and therefore of a peroximide; and, secondly, that its nitrogen is trivalent.

Among the facts bearing on its constitution as a peroxylamine, that is, as a derivative of $H_2NO{\cdot}ONH_2$, are, first, those of its mode of formation. The 2/3-normal hydroxylaminedisulphonate loses its two hydrogen atoms, at the ordinary temperature and when it is in aqueous solution, by the action of ozone, lead peroxide, silver oxide, and a variety of other substances:

$$(SO_3K)_2NOH + HON(SO_3K)_2 \rightleftarrows (SO_3K)_2NO{\cdot}ON(SO_3K)_2,$$

but not, however, by oxygen itself, for Raschig's observation, that a solution of hydroxylaminedisulphonate, when exposed to the air may assume a slight violet colour, applies in reality only to the case where the 2/3-normal salt is contaminated with nitrite, the pure salt never oxidising nor colouring in this way. The interaction with lead peroxide points clearly either to the peroxide constitution or, but with much less probability, to a rise in the combining power of the nitrogen to quadrivalency.

The fact of the ready reversion, at the common temperature and in solution, of a peroxylaminesulphonate to a hydroxylaminedisulphonate by acting as an oxidising agent is equally strong evidence of the same constitution. This reversion is also quantitative to an extent that admits of its being used to estimate the amount of the salt present in a solution (Schatzmann, Hantzsch and Semple).

Its combination with a molecule of normal sulphite (p. 13) affords convincing evidence to the same effect, since it is effected through the oxygen atoms of the peroxylaminesulphonate:

$$(SO_3K)_2NO{\cdot}ON(SO_3K)_2 + K{\cdot}SO_3K = (SO_3K)_2NOK + (SO_3K)ON(SO_3K)_2.$$

This interaction will be again discussed on page 20. Inferentially in favour of the peroxide constitution are also the odour which the peroxylaminesulphonates impart to the skin, their colour, and their decomposition into nitrous acid and sulphonated hydroxylamines.

So soon as it is recognised that peroxylaminesulphonates are peroxides, all doubt is removed as to the valency of their nitrogen, which then can be only that of a triad. Contrariwise, when such a constitution is not admitted, the nitrogen of a peroxylaminesulphonate, with equal certainty, cannot be trivalent. In order, therefore, to strengthen the conviction that the peroxylaminesulphonates are indeed peroxides and peroximides, it becomes important to state the reasons against admitting the nitrogen of these salts to be quadrivalent or more than trivalent.

To begin with, it is extremely improbable that oxidation by lead peroxide, silver oxide, or ozone should raise the valency of the nitrogen to only quadrivalency and not to quinquevalency, and that it should raise it at all without converting the sulphonate to sulphate radicals. Neither Claus nor Raschig assumes that it does, for according to them the nitrogen of the hydroxylaminedisulphonate is itself quinquevalent. But there are two strong reasons for rejecting the assumption that the valency of the nitrogen is raised by the oxidation of hydroxylaminedisulphonates to peroxylaminesulphonates. One of these is the nature of the products of the spontaneous decomposition of a peroxylaminesulphonate. These products, in so far as they contain nitrogen, are all trivalent nitrogen compounds, namely and in the main, hydroxylaminetrisulphonate, hydroxylaminedisulphonate, and nitrite ; if nitrous oxide is also recognised, that will not affect the argument. No nitrate can be found among these products (p. 36). It is, of course, the establishment of the trivalency of the nitrogen of the first-named product which has really settled the matter. But as it is only as yet on the chemical work of Divers and the author (this Journ., **7**, 34), that the adoption of the trivalency of the nitrogen in hydroxylaminedisulphonates can be based, the result of a determination by a cryoscopic method (p. 33) of the molecular magnitude of the normal sodium hydroxylaminedisulphonate may be adduced in support of it. This result shows that the molecule of the salt contains but one atom of nitrogen (necessarily therefore trivalent), and not two atoms as had been represented by Claus and by Raschig. Now, the spontaneous decomposition of a peroxylaminesulphonate can only be hydrolytic and, is therefore one not affecting the valency of the nitrogen ; or, should this be contested, it can still be asserted that at least this decomposition cannot be interpreted as a change involving a fall of the valency of the nitrogen.

The other reason against the belief that the valency of the nitrogen changes when a hydroxylaminedisulphonate is oxidised to a peroxylaminesulphonate is that of the production of the two compounds of trivalent nitrogen, the hydroxylaminedisulphonate and hydroxylaminetrisulphonate by the union of a peroxylaminesulphonate with a normal sulphite (p. 13). These two reasons for regarding the nitrogen of a peroxylaminesulphonate as trivalent seem to be conclusive and therefore support the view that these salts are constituted as peroxides or peroximides.

Since the sodium salt is even more unstable than the potassium salt, the determination of the molecular weight of a peroxylaminesulphonate has not been possible. It would seem better to modify Hantzsch and Semple's suggestion concerning the molecular weights of the two forms of the potassium salt (p. 3), to the extent of giving the simple formula, $(SO_3K)_4N_2O_2$, to the violet form, and reserving the double formula, or even a higher multiple of this, for the yellow form.

Products of Decomposition—Without further experiments than those described on pages 23 and 41, the number of the products and the great variations in their proportions are such that the nature of the spontaneous decomposition of a peroxylaminesulphonate cannot yet be fully determined. But its general character can be indicated, now that the constitution of both peroxylaminesulphonates and hydroxylaminetrisulphonates has been determined.

It can hardly be doubted that the molecule of peroxylaminesulphonate becomes halved by hydrolysis and converted into the hydroxylaminedisulphonate, always found in abundance, and the *hydroperoxylaminedisulphonate*, as yet undiscovered because incapable of continued existence, thus:

$$(SO_3K)_2NO\cdot ON(SO_3K)_2+H_2O=(SO_3K)_2NO\cdot OH+H\cdot ON(SO_3K)_2.$$

It is already known (this Journ **3**, 218 ; **7**, 40) that, in the presence of alkali, the nitroxy-radicals of a hydroxylaminesulphonate tend to separate from the sulphonate radicals. Such a tendency, exercised in the presence of undecomposed peroxylaminesulphonate, will lead to the production of hydroxylaminetrisulphonate and nitrite in the case of hydroperoxylaminesulphonate, and of the former salt and hyponitrite in the case of hydroxylaminedisulphonate, thus :

$$(SO_3K)_4N_2O_2+(SO_3K)_2NO.OH=2(SO_3K)_2NO(SO_3K)+HONO\ ;$$

$$(SO_3K)_4N_2O_2+(SO_3K)_2NOH\ =2(SO_3K)_2NO(SO_3K)+{}^1/_2(HON)_2.$$

When the three equations are combined, the intermediate products disappear and the following equation is left,

$$6(SO_3K)_4N_2O_2+H_2O=8(SO_3K)_3NO+2NO_2H+N_2O\ldots\ldots\ldots(\mathbf{1})$$

or, leaving the comparatively stable hydroxylaminedisulphonate unchanged,

$$2(SO_3K)_4N_2O_2+H_2O=2(SO_3K)_3NO+(SO_3K)_2NOH+NO_2H\ldots.(\mathbf{2})$$

It is fairly certain that the sulphate which, in greatly varying although never very large quantity, is always produced, does not come from the hydrolysis of the salt itself or from that of either the hydroxylaminetrisulphonate or hydroxylaminedisulphonate derived from it. For the trisulphonate is remarkably stable in presence of alkali, and the disulphonate, although unstable in its presence, yields not sulphate but sulphite. As this is also true of hydroxylaminemonosulphonate, it may be assumed to be so in the case of peroxylaminesulphonate. The sulphate should therefore have another origin, which may well be taken to be the decomposition of the hydroperoxylaminesulphonate in circumstances in which it fails to interact with peroxylaminesulphonate, perhaps because the temperature of the solution is too low. In that case, it will naturally hydrolyse, one half becoming hydroxylaminedisulphonate by oxidising the other half into sulphate and nitrous acid,

$$2(SO_3K)_2NO{\cdot}OH+H_2O=(2SO_4KH+NO_2H)+(SO_3K)_2NOH.$$

Or, it may well hydrolyse wholly into sulphate and nitrous oxide,

$$2(SO_3K)_2NO{\cdot}OH+H_2O=4SO_4KH+N_2O.$$

These equations combined with the primary equation give,

$$2(SO_3K)_4N_2O_2+3H_2O=2SO_4KH+3(SO_3K)_2NOH+NO_2H\ ;\ldots(3)$$

$$2(SO_3K)_4N_2O_2+3H_2O=4SO_4KH+2(SO_3K)_2NOH+N_2O\ldots\ldots(4)$$

An equation to account for the production of nitrogen, and another for that of aminemonosulphonate are easily framed :

$$(SO_3K)_4N_2O_2+2H_2O=4SO_4KH+N_2\ ;\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$(SO_3K)_4N_2O_2+3H_2O=3SO_4KH+(SO_3K)NH_2+NO_2H.\ \ldots\ldots(6)$$

A justification of the lower of these equations and an illustration of the nature of the change expressed by it are to be found in the production of aminemonosulphonate from hydroxylaminedisulphonate when decomposing in presence of copper sulphate (this Journ., **13** 497).

By combining these six equations in different ways, the various results obtained can be explained (p. 42), although the conditions for the occurrence of one mode of decomposition more than another are not yet ascertained.

Sabatier's Bluish-violet Acid.—Sabatier has studied the nature of the bluish-violet colour produced in a solution of nitrososulphuric acid (nitrosyl hydrogen sulphate) in the monohydrate of sulphuric acid by sulphur dioxide, and in other ways (*loc. cit.* p. 3); and has found this colour to be more closely like that of a solution of potassium sulphazilate than the colour of the latter is like that of a solution of potassium permanganate. On this ground and from a consideration of the circumstances which give rise to it, he has suggested that it is due to the presence in the solution of the acid of Fremy's salt, constituted according to the formula, $ON(SO_3H)_2$. Sabatier may be right, but there is much to be said against this opinion. Firstly, the tints of the two coloured solutions are not so similar as he asserts. Secondly, certain striking contrasts may be observed in the chemical character of the two solutions. Potassium peroxylaminesulphonate is produced by the action of lead peroxide and is not attacked by it, whereas the coloured acid solution is at once oxidised by lead peroxide. Conversely, whilst this acid solution is indifferent towards sulphur dioxide and produced by it, potassium peroxylaminesulphonate is at once changed by this reagent.

Then, again, it has not proved to be possible to convert potassium peroxylaminesulphonate into this violet acid solution or to effect the opposite change. Mr. S. Sekiguchi, a Post-graduate of this University, has kindly carried out some experiments in this direction. Making the mixtures very gradually and keeping them cold by ice and salt, he has poured the solution, prepared from nitrososulphuric acid and sulphur dioxide in sulphuric acid, into a solution of potassium hydroxide; and, on the other hand, an aqueous solution of potassium peroxylaminesulphonate into some concentrated sulphuric acid; in both cases, an almost immediate disappearance of the violet colour results. In the former case, too, the alkaline solution was evaporated and crystallised, without finding any of the hydroxylaminetrisulphonate which would result from the decomposition of peroxylaminesulphonic acid and might, to some extent, in accordance with its usual stability, escape decomposition.

Details of Experiments.

The Exhaustive Action of Lead Peroxide on Hydroxylaminesulphonates.

2/3-normal potassium hydroxylaminedisulphonate was boiled with excess of lead peroxide in about 15 times its weight of water, containing from 1/5 to 2/5 of a molecule of potassium hydroxide, until the solution had again become colourless. To the cold filtrate, just enough barium acetate was added, to precipitate all sulphate present; the filtrate was then evaporated, and the hydroxylaminetrisulphonate crystallised out as far as possible and weighed. Potassium nitrite, produced in large quantity, was estimated in the mother liquor and alcoholic washings of the crystals of the hydroxylaminetrisulphonate by the urea method. Sulphate was found partly in solution and partly in the lead residue, which was extracted alternately with dilute nitric acid and potassium hydroxide. The sulphate, both in solution and residue, was estimated and, in two cases, the soluble lead also, as a measure of lead peroxide consumed.

In one experiment, 73·2 grams of salt gave 58·2 grams of trisulphonate in crystals, that is, 58·5 mol. of trisulphonate from 100 mol. of disulphonate, or 87.75 per cent. of the theoretical quantity. Nothing else was determined, and so high a yield of hydroxylaminetrisulphonate was only reached by adding alcohol to separate the last portions of the salt from the very concentrated nitrite mother liquor.

In another experiment, 125 grams of the disulphonate gave 97·33 grams of trisulphonate, equal to 57·33 mol. of trisulphonate to 100 mol. of disulphonate, or 86 per cent. of the calculated quantity. The amount of potassium sulphate was 21·5 mol. per 100 mol. of salt taken, which leaves sulphur for the trisulphonate equivalent to 59·5 mol., as against the 57·33 mol. of crystallised salt. Very much nitrite was found, 37·5 mol. per 100 mol. of disulphonate taken, indicating the production of very little nitrous oxide. The only way to interpret this large production of nitrite is to assume that, whilst 89·25 per cent. of the salt was oxidised into trisulphonate and nitrite, and only 3 per cent. into sulphate and nitrous oxide, 7·75 per cent. was oxidised into sulphate and nitrite, an assumption which cannot be easily justified.

In an earlier experiment, in which the crystallisation of the trisulphonate was only imperfectly carried out, 136·33 grams of the disulphonate gave 84·33 grams of the crystalline product that is, 100 mol. gave 45·56 mol., or 68·33 per cent. of the theoretical quantity. But, since the quantity of sulphate, almost if not actually the only other sulphur compound produced, amounted to only 19 mol. per 100 of disulphonate, the actual yield of trisulphonate can have been little short of 60·33 mol. per 100. The nitrite, as determined by the urea method, was 28·4 mol. per 100 of disulphonate taken. But the lead peroxide consumed was in this case determined, and made out to be 71·5 mol. per 100 mol. disulphonate, and this indicates the production of 31·8 mol. nitrite. Accepting the mean of these numbers for the nitrite, it results that about 90 per cent. of the hydroxylaminedisulphonate was converted into trisulphonate and nitrite, and the rest into sulphate and nitrous oxide.

In an experiment with 35 grams of potassium hydroxylaminedisulphonate, in which the crystals of hydroxylaminetrisulphonate were not weighed, 100 mol. yielded 13 mol. of sulphate and 26 mol. of nitrite. Calculating from these quantities, 78 per cent. of the salt was oxidised into trisulphonate and nitrite, 15·5 into trisulphonate and nitrous oxide, and 6·5 into sulphate and nitrous oxide. The trisulphonate produced will therefore have been about 93·5 per cent. of the calculated quantity, or 62·33 mol. per 100 mol. disulphonate.

Another experiment was made on the normal sodium hydroxylaminedisulphonate (this Journ. **7**, 49) in dilute solution, 11·33 grams being taken without adding sodium hydroxide, because the alkalinity of the salt was sufficient to protect it. But in this experiment, only the quantities of lead peroxide consumed and of sulphate formed were estimated. Exactly as happened in the experiment with the potassium salt, 71·5 mol. of lead peroxide were consumed per 100 mol. sodium salt. The sulphate amounted to 34 mol. per 100 mol. of salt used, more, that is, than in the experiments with the potassium salt. The calculated quantity of sodium hydroxylaminetrisulphonate was correspondingly lower, 55 mol. per 100 mol. or 82·75 per cent. of the theoretically possible quantity.

Reduction of Potassium Hydroxylaminetrisulphonate by Sodium Amalgam.—In the interaction between sodium amalgam and potassium hydroxylaminetrisulphonate in aqueous solution, the two liquids become warm and the action is soon over, if the two are well shaken together. No gas is evolved, and nothing is left in solution but the two salts, sulphate and aminedisulphonate (iminosulphate). The latter is easily recognisable by its separating as the very sparingly soluble 2/3-normal potassium salt when the solution is nearly neutralised with an acid, and also by its nearly insoluble normal mercury-potassium salt (this Journ. **6**, 96 ; **9**, 210). But the salt was also analysed quantitatively (p. 28) in order to demonstrate its nature beyond question. By cautiously adding hydrochloric acid to the cold solution until it has become almost neutral to methyl-orange and then precipitating with barium chloride, the sulphate is partially separable from the aminedisulphonate. The latter may then be estimated as sulphate in the filtrate after hydrolysis at 150°. In an experiment carried out in this way upon 2·447 grams of potassium hydroxylaminetrisulphonate, the barium sulphate was washed with cold and then with hot water, ignited, and weighed. The sulphate from the hydrolysed aminedisulphonate was treated as in an ordinary sulphate determination. In this way determined, 34·79 per cent. of the sulphur came out as sulphate and 64·88 per cent. as aminedisulphonate, leaving 0·33 per cent. unaccounted for. In accordance with the equation, the actual numbers should have been 33·33 and 66·67 per cent. respectively. By other experiments it was, however, established that some of the aminedisulphonate was precipitated with the sulphate. No doubt, also, some barium chloride was carried down.

Potassium hydroxylaminetrisulphonate, 1·441 grams, was reduced by sodium amalgam, and the solution neutralised and precipitated in the cold by barium chloride as above described. The washed precipitate was then heated for four hours at 150° with dilute hydrochloric acid in a sealed tube. The acid was nearly neutralised, and the barium sulphate collected, washed, and weighed as usual. The filtrate from this yielded a fresh precipitate with barium chloride, for the barium aminedisulphonate, which was precipitated with the sulphate, had been hydrolysed into barium sulphate and ammonium hydrogen sulphate. Therefore, from the weight of the main precipitate of sulphate was deducted that of the small quantity last obtained, and the remainder taken as sulphate actually produced by the sodium reduction. It amounted to the equivalent of 34·20 per cent. of the total sulphur. The aminedisulphonate in the original filtrate from crude sulphate was determined by hydrolysing and weighing its sulphur as sulphate. To the weight of this was added twice that of the barium sulphate obtained, as just described, from the soluble sulphate extracted by hydrolysing the crude barium sulphate, because twice that quantity represented the total sulphur of the aminedisulphonate precipitated along with the sulphate. This sum was equivalent to 65·75 per cent. of the total sulphur. That these data still deviate from the calculated numbers is no doubt due to the adsorption of a little barium chloride to the sulphate when precipitated in the cold. The barium of this chloride will have rendered insoluble some of the sulphate which should have dissolved out through the hydrolysis of the aminedisulphonate simultaneously precipitated. There seems, therefore, to be no reason for doubting the quantitative accuracy of the equation given on page 6.

An experiment was then tried to see whether closer results could not be got by removing as much as possible of the aminedisulphonate from the solution before precipitating the sulphate, first crystallising out most of it from the nearly neutralised solution, and then removing some of the remainder as the mercury-potassium salt, by digesting the solution with mercuric oxide. This method, however, did not give better results than the preceding.

Reduction of Potassium Hydroxylaminetrisulphonate by the Zinc-copper Couple.——The reduction of the trisulphonate was successfully effected by boiling its solution, (to which a few drops of solution of sodium acetate had been added in order to protect the salt from hydrolysis) with some zinc-copper couple. But in consequence of the necessity of boiling the solution, hydrolysis of the aminedisulphonate is apt to set in.

Some aminedisulphonate, prepared by the sodium amalgam method and another sample, prepared by the zinc-copper couple were analysed with the following results :

	By sodium.	By zinc-copper.		Calc.
Potassium	30·68	30·72	———	30·89
Sulphur	25·09	24·85	25·94	25·30
Nitrogen	5·32	6·16		5·54

Hydrolysis of a Hydroxylaminetrisulphonate.—— The complete hydrolysis of the hydroxylaminetrisulphonates is more difficult to effect than that of any other of Fremy's salts. In the quantitative analysis of the salts, it was found necessary to keep the acidified solution for five hours at 180—200°. In the case of the potassium salt, the mean percentage of sulphur then came out as 23.18 ; at

150° only, for four hours, it was 22·85 ; and at 90—100° for five hours and then three hours at 130,° it gave only 22·64. In this case, the nitrogen of the hydroxylamine obtained (as measured by the iodine method) amounted only to 2·5 per cent.. In another case, where the hydrolysis was allowed to go on for 48 hours at 90-95° and then 2 hours at 130-134°, the nitrogen obtained as hydroxylamine was 2·71 per cent. (79·75 per cent. of total nitrogen).

Inactivity of Sulphites towards Hydroxylaminetrisulphonates.—Potassium hydroxylaminetrisulphonate weighing 2 grams, in sufficient water to keep the salt in solution, was left for 3 days with 3 grams of potassium metasulphite, rendered slightly alkaline to lacmoid paper (whilst strongly acid to litmus). The sulphite was then precipitated by barium hydroxide and the filtrate evaporated. In this way 1.98 grams of the hydroxylaminetrisulphonate were crystallised out. The analysis of the salt thus recovered is given as that of II among the analyses of the salt below.

Analysis of Potassium Hydroxylaminetrisulphonate.—Although this has been analysed by previous workers, it was necessary to make several careful and full analyses in order to establish the fact that it contains more water of crystallisation than the proportion stated by Claus and by Raschig. Four separate preparations were analysed.

I. 0·4954 g. substance gave 0·3117 g. potassium sulphate; 0·5088g. gave 0·8581g. barium sulphate; 0·3387g. gave 0·5680g. barium sulphate; 0·2821g. substance, finely powdered and heated in a current of dried air, first at 95° and then up to 110°, lost 0·0138g.; 0·2174g. lost in this way 0·0101g.

II. 0·2272g. substance gave 0·1429g. potassium sulphate; 1·0676g. treated with sodium amalgam for 24 hours and then hydrolysed at 150° for 3 hours, gave 1.7918g. barium sulphate and ammonia=25.59c.c. N/10 acid.

III. 0·2288g. substance gave 0·1451g. potassium sulphate ; 0·1003g. gave 0·1710g. barium sulphate.

IV. 0·8505g. substance gave 0·5347g. potassium sulphate ; 0·34475g. gave 0·5799g. barium sulphate ; 2·4425g. by sodium amalgam treatment and hydrolysis at 150° for 3 hours, gave ammonia=51·38c.c. N/10 acid ; 0·7650g. by the Dumas method gave 22·3.c.c moist nitrogen at 16° and 758mm.

		Potassium.	Sulphur.	Nitrogen.	Water.
Found ;	I.,	28·25	23·18 23·05	—— ——	(4·89) (4·65)
,,	II.,	28·24	23·07	3·37	——
,,	III.,	28·47	23·42	——	——
,,	IV.,	28·23	23·12	(2·95) 3·39	—— ——
Meaa,		28·30	23·18	3·38	(4·77)
Calc. for	1/1 H_2O,	28·95	23·71	3·46	4·49
,,	3/2 H_2O,	28·32	23·19	3·39	6·52
Fremy,		28·02	23·40	3·48	——
Claus, found (taking old at opnic. weights.)					
		28·63	——	3·24	5·04
,,	,, ,,	28·55	——	——	5·20
,,	,, ,,	28·67	23·69	——	5·01
,,	,, ,,	28·79	23·76	3·31	4·71
Claus, mean,		28·66	23·73	3·28	4·99
,,	calc. (old at. wts.),	28·88	23·70	3·45	4·44
Raschig,		28·47	23·64	——	——
,,		28·54	23·38	——	——

Claus has also given the results of five closely concordant analyses of the anhydrous salt, and should therefore have experienced no difficulty in rendering it anhydrous. In the attempts to determine total water, recorded above, the residue was always acid in consequence of unavoidable hydrolysis and fixation of some of the water of crystallisation. A discussion of this matter is given on page 8.

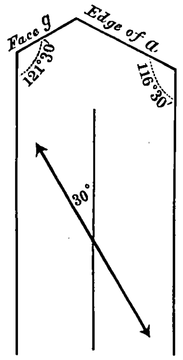
Analysis of the Sodium Salt.—Two distinct preparations of the sodium salt were analysed :

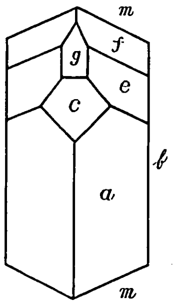
I. 0·4910 g. substance gave 0·2801 g. sodium sulphate; 0·3845 g. gave 0·7174 g. barium sulphate, after hydrolysis at 200° for 3 hours. Hydrolysed at only 160° for 5 hours, 0·4548 g. gave 0·8378 g. barium sulphate, = sulphur 25·30 per cent. only.

II. 0·6097 g. substance gave 0·3455 g. sodium sulphate; 0·1750 g. gave 0·3268 g. barium sulphate, after hydrolysis at 210° for 3 hours ; 0·7533 g. gave 24·0 c.c. moist nitrogen at 760·8 mm. and 17°, = 0·0279 g. nitrogen.

	Sodium.	Sulphur.	Nitrogen.
Found, I.,	18·50	25·64	——
,, II.,	18·36	25·67	3·70
$Na_3S_3NO_{10}, 2H_2O$,	18·42	25·62	3·76

Crystallography of Sodium Hydroxylaminetrisulphonate.—Professor Jimbō has kindly given me the following description of the crystals of this salt, which were examined under his directions by Mr. Y. Ōtsuki, University Post-graduate. Thick, tabular, monoclinic crystals, about 3 mm. long and 2 mm. wide, elongated in the direction of the vertical axis. The observed faces are of seven kinds, of which *b* is the largest and apparently the plane of symmetry. *m*, making with *b* an angle of about 115°, may be taken as a prism ; *d*, *e*, and *f* as pyramids ; *c* as the base, and *g* as a positive orthodome. Two other faces in the zone of the orthodiagonal are sometimes observed. A crystal laid flat on the clinopinacoid shows an extinction angle of 30° to the vertical axis, in the acute angle between this and the clinodiagonal.





Analysis of the Ammonium Salt.—

0·3005 g. substance gave 0·6045 g. barium sulphate, after hydrolysis at 195° for 5 hours; 0·1207 g. gave 16·57c.c. moist nitrogen at 763 mm. and 15° C.

	Found.	$2H_{12}O_{10}N_4S_3,3H_2O$.	$H_{12}O_{10},N_4S_3H_2O$.
Sulphur	27·63	27·36	28·08
Nitrogen	16·06	15·98	16·40

Analysis of the Basic Lead Salt.—The salt was dried for analysis in a current of dried air at 100° in the case of preparation I, and at 110° in that of II. The salt was quite free from potassium but contained a trace of acetate.

I. 0.4441 g. substance gave 0.3560 g. lead oxide and 0.1936 g. barium sulphate.

II. 0.3775 g. substance gave 0.4098 g. lead sulphate.

		Found.		Found.	$O_{16}NS_3Pb_6,3H_2O$
Lead	I.	74·41	II.	74·14	74·71
Sulphur		5·99		——	5·79

Determination of the Molecular Magnitude of Sodium Hydroxylaminetrisulphonate.—This was carried out by Löwenherz's method with melted sodium sulphate crystals (*Zeit. physikal. Chem.*, 1896, **18**, 70) and using hydrated sodium hydroxylaminetrisulphonate. Sodium sulphate gets by dissolution in it of the hydrated hydroxylaminetrisulphonate a little more water than corresponds to the hydrate with 10 molecules of water, but the crystalline sulphate separates the anhydrous salt in abundance on fusion, and as the crystallising temperature of the melted salt does not change as long as the anhydrous salt remains at the bottom, this additional water is only equivalent to the use of a slightly greater quantity of the crystallised salt. A correction was, therefore, introduced by calculating from this additional water the corresponding quantity of hydrated sodium sulphate.

Hydrated salt	Anhydrous salt	Glauber's salt taken.	Glauber's salt corrected	△t	M. W.
$O_{10}NS_3Na_3 \cdot 2H_2O$					
2·479g	2·2411g	58·985g	59·411g	0·369°	332·2
3·3417g	3·0210g	56·946g	57·520g	0·510°	335·6

$O_{10}NS_3Na_3$ requires 339.4

Molecular Magnitude of Normal Sodium Hydroxylaminedisulphonate.

Hydrated salt.	Anhydrous salt.	Glauber's salt taken.	Glauber's salt corrected.	△t	M. W.
$N_aON(SO_3N_a)_2.3H_2O$					
1·2200g	1·0093g	36·818g	37·198g	0·39°	233·2
2·4455g	2·0230g	36·442g	37·198g	0·74°	239·6

$O_7NS_2Na_3$ requires 259·3

Solubility of Peroxylaminesulphonate in N/10 Solution of Potassium Hydroxide.—The purified salt, previously washed on the porous tile with some of the solvent, was shaken with it for from 15 to 20 minutes, the temperatur of the solution being 29°. After some time 5 c.c. of the clear solution were pipetted off. The rest of the solution, along with the undissolved salt, was left for some hours in ice, when again 5 c.c. were taken out, the temperture being then 3°. The two portions were each weighed and the amount of dissolved salt ascertained by a sulphur determination. It was thus found that 0·163gram of salt was dissolved in 5·03 grams of its alkaline solution at 29°, and that 0·027 gram was dissolved in 4·98 grams of its solution at 3°.

Interaction of Potassium Peroxylaminesulphonate and Normal Potassium. Sulphite—To a solution of 3.6 grams of potassium peroxylaminesulphonate, containing a very small quantity of potassium hydroxide, a solution of normal potassium sulphite (neutral to phenolphthalein) was added from a burette, with constant stirring, until the violet colour of the solution was entirely discharged. The change took place quickly but not instantly. The quantity of sulphite required was only a little more than that indicated by theory. After a short interval, baryta water was added to precipitate the excess of sulphite and the hydroxylaminedisulphonate. The excess of baryta was removed from the filtered solution by carbon dioxide and the filtered solution evaporated so as to get out as much as possible of the sparingly soluble potassium hydroxylaminetrisulphonate. Some more of this salt was precipitated by adding twice the volume of alcohol and leaving the mixture for some time. The total trisulphonate thus separated weighed 2·268 grams, or 81·5 per cent. of the calculated quantity.

The barium precipitate was triturated in a mortar with very dilute acetic acid, added very slowly so as to avoid as far as possible having any local excess of acid. When the solution had become neutral to phenolphthalein, the undissolved barium sulphite was filtered off. Potassium carbonate in slight excess was added and the whole left to stand for a day. Then, the solution, filtered from the barium carbonate and neutralised with acetic acid, was concentrated in a vacuum over sulphuric acid and mixed with twice its volume of alcohol. In 12 hours, the quantity of precipitated crystalline 2/3-

normal hydroxylaminedisulphonate weighed 1·55 grams, this being equal to 76 per cent. of the calculated quantity. It was pure, except for a trace of aminetrisulphonate (nitrilosulphate), doubtless due to the action of the sulphurous acid unavoidably liberated in the process of separating the barium sulphite from its own barium salt by acetic acid. It was identified by hydrolysis into sulphate and hydroxylaminemonosulphonate, and above all by its producing the bluish-violet peroxylaminesulphonate when warmed with lead peroxide and a small quantity of alkali. No nitrite was found in the mother liquor of the hydroxylaminetrisulphonate, showing that the production of the latter salt had not been due to spontaneous decomposition of the peroxylaminesulphonate. Hydroxylaminetrisulphonate and disulphonate are, in fact, the only substances which could be detected among the products of the interaction of the peroxylaminesulphonate and sulphite. Since, therefore, the separated quantities of these products were found to be in approximately molecular proportions, and as these salts are not insoluble, even in their alcoholic mother liquors, it may be regarded as proved that the interaction which takes place is exclusively that represented by the equation on page 18.

Spontaneous Decomposition of Potassium Peroxylaminesulphonate.— The principal products of the spontaneous decomposition of a peroxylaminesulphonate in hot alkaline solution are easy to recognise. Unless very dilute, the solution yields crystals on cooling and more on evaporation. At first the sparingly soluble hydroxylaminetrisulphonate alone crystallises, and later on both this and the equally sparingly soluble hydroxylaminedisulphonate. In each case the crystals are characteristic and easily distinguished. The presence of the disulphonate in the solution is quickly and distinctively indicated, as has just been mentioned, by warming with a small quantity of lead peroxide, which gives it again the bluish-violet colour of peroxylaminesulphonate. By removing sulphate and hydroxylaminedisulphonate from the solution by barium hydroxide, nearly all the hydroxylaminetrisulphonate can be crystallised out; the mother liquor containing the nitrite may then be tested in any of the usual ways for this salt.

It was important to know whether any nitrate is formed by the decomposition, and therefore necessary first to get rid of all the nitrite present by a process that does not convert any of it into nitrate. The nitrite was accordingly changed into aminetrisulphonate (nitrilosulphate) by adding enough potassium carbonate and then passing in sulphur dioxide until the solution became acid, at which point the aminetrisulphonate that had been produced at once hydrolysed (this Journal **6**, 65). Lastly, by blowing in air until all the remaining sulphur dioxide had been expelled, the acid solution was left free from either nitrite or sulphite, and, therefore, ready for testing for nitrate. None of this salt was found. The application of the process of sulphonating the nitrite to the determination of total nitrogen in solution, is described on page 39).

The testing for aminemonosulphonate (aminosulphate) among the products of decomposition of a peroxylaminesulphonate is not an easy matter. The method adopted was to oxidise all the hydroxylaminedisulphonate by boiling the solution with lead peroxide until it was again colourless. The nitrite was then oxidised by pouring the solution into potassium permanganate solution to which sulphuric acid had been added. Mercuric nitrate solution then precipitated from it a little oxymercuric aminemonosulphonate (this Journal, **9**, 242), which, when treated with hydrogen sulphide, left the acid again in solution. By evaporation and addition of strong sulphuric acid, the acid was obtained in characteristic crystals (*loc. cit.*, 229), which were sometimes weighed.

The quantitative examination of the solution is a troublesome and less satisfactory operation. The peroxylaminesulphonate can hardly be obtained for weighing in the dry and pure state, because of its instability. Therefore, after its composition had been found, from concordant analyses of four different preparations, to be that ascertained by previous workers, the preparation of the solution and its analysis after the salt had all decomposed were carried out in the following way. The peroxylaminesulphonate, recrystallised two or three times from hot water made alkaline with potassium hydroxide, was drained a short time on a tile from its mother liquor, and at once dissolved in suitable quantity in water to which had been added a measured quantity of potassium hydroxide. The solution was maintained at the boiling temperature until colourless through the complete decomposition of the salt. The cold solution was weighed off into four portions ; one of 5 per cent. of the whole, for estimating the amount of peroxylaminesulphonate that had been dissolved ; another of 15 per cent., for estimating the quantity of hydroxylaminetrisulphonate produced ; a third and a fourth portion, each of 40 per cent., for estimating in one the quantity of sulphate and in the other that of nitrite produced. The quantity of peroxylaminesulphonate taken was determined by weighing as barium sulphate the total sulphur in the solution. To ensure the hydrolysis of all the sulphonate, the solution was heated with the hydrochloric acid in sealed tubes for 4-5 hours at 180°-200°.

To determine the quantity of sulphate which had been produced, very dilute hydrochloric acid was added with constant stirring until the solution was left only barely alkaline to phenolphthalein, then much ammonium chloride was added before precipitating with barium chloride, in order to keep the hydroxylaminedisulphonate in solution as far as possible. The impure sulphate, washed with ammonium chloride solution on the filter, was transferred to a beaker and digested in the cold with very dilute hydrochloric acid, washed again on the filter with boiling water, and then ignited in the usaul way.

The hydroxylaminetrisulphonate was estimated by leaving the solution with sodium amalgam for two days, occasionally shaking the two together, so as to convert this salt into hydroxylaminedisulphonate, and then all the hydroxylaminedisulphonate in the solution into aminedisulphonate (iminosulphate). The mercury having been filtered off and washed, hydrochloric acid was added to the solution until it was only just alkaline to methyl-orange, and then an excess of ammonium chloride was introduced. The sulphate was finally precipitated and treated as before described. Deducting from this quantity of sulphate that which was present before the treatment with sodium amalgam, there remained the sulphate equivalent to one-third of the sulphur of the hydroxylaminetrisulphonate, from which the quantity of this salt was calculated. Assuming hydroxylaminedisulphonate to be the only other sulphur compound produced in the decomposition of the peroxylaminesulphonate—an assumption nearly exact—the amount of this salt was then calculated as being equivalent to the sulphur not found either as sulphate or hydroxylaminetrisulphonate. The slight error in this assumption is caused by the production of very small quantities of aminemonosulphonate (aminosulphate). As to the last-named salt, it has not been possible to do more than ascertain that its quantity is usually quite small, although 2 mol. of the crystalline acid (p. 36) per 100 mol. of hydroxylaminedisulphonate oxidised by the lead peroxide were once actually obtained. In other words, the amount of the sulphur found as aminemonosulphonate was in this instance 1·03 per cent. of that of the hydroxylaminedisulphonate used.

To determine the total nitrogen in the solution, the nitrite was completely sulphonated to aminetrisulphonate (nitrilosulphate) by adding enough potassium carbonate for the purpose and then passing in sulphur dioxide until a piece of lacmoid-paper was just reddened (this Journ., **6**, 65). Next, the hydroxylaminetrisulphonate in the solution was reduced by sodium amalgam, as above described, to sulphate and aminedisulphonate. Having thus brought all the nitrogen to the state of aminesulphonates, the hydrolysis of these substances by hydrochloric acid was effected by heating, first, on the water-bath until all the sulphur dioxide had been expelled, and then for some hours in a pressure-tube at 150°. The solution distilled with alkali gave up all its nitrogen as ammonia. The difference between this and that originally present as peroxylaminesulphonate gives, indirectly, the quantity of nitrogen in the gases, whilst the difference, again, between the total nitrogen in the solution and the sum of the quantities found as disulphonate and trisulphonate is the nitrogen which was present as nitrite.

Although the experimental work in estimating sulphate and hydroxylaminetrisulphonate was performed with great care, no high degree of accuracy in the results could be expected. A test experiment was made to see to what extent the method was imperfect. A solution was prepared by dissolving potassium sulphate, potassium hydroxylaminetrisulphonate, potassium hydroxylaminedisulphonate, and sodium nitrite in water to every 100 c.c. of which 5 c.c. of N/10 solution of potassium hydroxide had been added. The solution was twice analysed for sulphate and trisulphonate, in the way described above. The quantities, taken and found, are here given in grams per 100 c.c.

	Taken.	Found.	
Trisulphonate,	2·580	2·547	2·624
Sulphate,	·347	·380	·373
Disulphonate,	·622	·629	·551
Nitrite,	·208	·212	·217

From this experiment, it seems that the sulphate may come out nearly 10 per cent. too high, no doubt for two reasons; one that, being precipitated in the cold, the barium sulphate retained other salts with it; the other and principal reason being that, in the process of neutralising the solution, some of the disulphonate must be decomposed, yielding sulphate. The numbers for the trisulphonate are much more satisfactory, being less than 1.7 per cent. too high, apparently because they represent the difference between two sulphate determinations, the error in the one counterbalancing the corresponding error in the other. When, however, we come to the numbers for the disulphonate, which are calculated from those for the other substances, it is seen how large the error may become, being in one case as much as 11·4 per cent. too low. Similarly, the quantity of nitrite calculated from those of the other substances may come out as much as 4·5 per cent. too high. The expression of the errors as percentages only holds good, of course, where the salts in an actual experiment are nearly in the same proportions as here taken, as they were generally found to be.

The quantities of nitrite and of gases yielded by the peroxylaminesulphonate may also be each determined directly. The nitrite may be estimated by the urea method, as stated on page 24, most of the sulphonate salts having first been crystallised out and washed with alcohol. The method for collecting and measuring the gases produced during the decomposition consists in letting this proceed in a closed vessel from which the air is withdrawn. A stout-walled, cylindrical bolt-head, of about 250 c.c. capacity, with a stopcock sealed on to it, was exhausted and then opened with its mouth in the solution of peroxylaminesulphonate and potassium hydroxide. About 200 c.c. were allowed to enter, holding between 6 and 7 grams of the salt in solution. The tube was again exhausted and the stopcock being then closed, the salt was decomposed by heating the solution. When cold, the apparatus was connected with a Sprengel-pump and the gases drawn off and measured. They proved to be free from nitric oxide, but, on treatment with strong alcohol, a small proportion of nitrogen remained undissolved. The experiments with this method of determining the gases have been very few and not such as have admitted of their utilisation in this paper, beyond giving proof that nitrogen in small quantity is generated along with the nitrous oxide, which is the main constituent of the gaseous mixture, and that the quantity of the gases may vary greatly in different experiments.

Where the decomposition of the peroxylaminesulphonate proceeds in the presence of lead peroxide, as it is made to do in the preparation of hydroxylaminetrisulphonate, no hydroxylaminedisulphonate can remain in the solution, and in place of it is found principally an increase in the quantities of trisulphonate and nitrite. The absence of the disulphonate simplifies the analysis as is seen on page 23.

Eight analyses of the products of the spontaneous decomposition of the peroxylaminesulphonate were made. In Expt. 1, a solution holding 2.3184 grams of potassium peroxylaminesulphonate and 60 c.c. of N/10 solution of potassium hydroxide was made up to 150 c.c. and then found to weigh 150.79 grams. It was slowly heated to the boiling point, and kept boiling till decolorised. Expt. 2.—The solution weighing 234.3 grams and containing 2·547 grams of the salt and 72·3 c.c. of N/10 potassium hydroxide was left in the cold for two days, and then boiled till colourless. During the boiling a reflux condenser was used to retain the water in the solution. Expt. 3.—A solution weighing 120.42 grams and measuring 120 c.c. of 1·22 grams of salt and 11·4 c.c. of N/10 potassium hydroxide was decomposed by boiling. Expt. 4.—The solution weighed 134.9 grams and contained 1·8576 grams of salt and 30 c.c. of N/10 potassium hydroxide ; it was decomposed by boiling. Expt. 5.—A solution of 0.6601 grams of salt and 20 c.c. of N/10 potassium hydroxide, weighing 34·25 grams, was left in the cold for a week, when it had become colourless. Expt. 6—Like the last, but the solution weighed 266·7 grams and the salt 5·27 grams, whilst the potassium hydroxide was taken in about the same proportion as before. Expt. 7.—The solution was a portion of the same as had been used for Expt. 2. When kept in a closely stoppered flask, it had only lost all its colour after about five months. Expt. 8.—This experiment differed from the others in the use of baryta-water in place of potassium hydroxide, and to this must be attributed the production of so much sulphate and hydroxylaminedisulphonate. The solution took a month to lose all its colour.

In the table, the numbers of molecules of the several products yielded by $100(SO_3K)_4N_2O_2$ are given according to calculation from the analyses made in the way above described, and without any corrections for the probable, but variable, errors inherent in the method.

Mol. weight.	1.	2.	3.	4.	5.	6.	7.	8.
$(SO_3K)_3NO$,	85	102·3	101·7	77·7	91·4	85·3	86	12·9
$(SO_3K)_2NOH$,	61	30	23·6	65·4	42·3	42	40·4	133·2
SO_4KH,	23	33	47·6	36	41·2	60	61·2	94·7
HNO_2,	49	36	32·5	50·2	35	37	26·4	—

Without further experiments, it does not seem possible to account for the wide variations in these numbers, except where baryta was used. From Expts. 2 and 7, started on portions of the same solution, it seems clear that, with the slow decomposition of the peroxylaminesulphonate which goes on in the cold, instead of the rapid change which occurs at a boiling heat, molecular quantities of hydroxylaminedisulphonate and sulphate take the place of some of the hydroxylaminetrisulphonate, and that a little of the hydroxylaminedisulphonate is replaced by its equivalent of sulphate and nitrous oxide. This becomes more obvious when equations in these two cases are given with only 12 molecules instead of 100 molecules of decomposing peroxylaminesulphonate. This is possible without deviating from the numbers found more than the imperfections of the analytical method allow.

$$(2).\quad 12(SO_3K)_4N_2O_2+6H_2O=12(SO_3K)_3NO+4(SO_3K)_2NOH+4SO_4KH+4NO_2H+2N_2O.$$

$$(7).\quad 12(SO_3K)_4N_2O_2+8H_2O=10(SO_3K)_3NO+5(SO_3K)_2NOH+8SO_4KH+3NO_2H+3N_2O.$$

The production of small quantities of nitrogen and aminemonosulphonate is of necessity ignored in the above calculations.

The author gratefully acknowledges his indebtedness to Dr. Divers. F. R. S., for a thorough revision of his manuscript.