LXXXII.—*Imidosulphonates.*

By EDWARD DIVERS, M.D., F.R.S., and TAMEMASA HAGA, F.C.S.

THIS paper gives the results of an investigation of the hitherto unknown sodium imidosulphonates and their derivatives, as well as of some new ammonium and potassium salts. In addition, several mixed tribasic salts which show peculiarities in their constitution are described, particularly those of lead, of silver, and of mercury. A description is also given of the experimental determination of the nature of Rose's "sulphatammon," a compound of 1 mol. of sulphur trioxide with 2 mols. of ammonia.

History.—Rose (1834—1840; *Ann. Phys. Chem.*, **32**, 81; **47**, 471; **49**, 183); Jacquelain (1843; *Ann. Chim. Phys.* [3], **8**, 293); Fremy (1845; *ibid.* [3], **15**, 408); Woronin (1859; *J. Russ. Chem. Soc.*, **3**, 273); Claus and Koch (1869; *Annalen*, **152**, 336); Berglund (1875;

L. univ. Arsk., **12** and **13**; *Bull. Soc. Chim.*, **25**, 455; **29**, 422; *Ber.*, **9**, 252 and 1896); Raschig (1887; *Annalen*, **241**, 161); and Mente (1888; *ibid.*, **248**, 232) are the chemists who have examined the inorganic salts now known as imidosulphonates.* The constitution of these salts has been established mainly through investigations by Rose, Jacquelin, and Berglund.

In 1834, Rose discovered that when the compounds of sulphur trioxide with ammonia, which he called "sulphatammon" and "parasulphatammon," are freshly dissolved in water, they give the reactions of a sulphate very incompletely or not at all, and do not yield up all their nitrogen as ammonia to chloroplatinic acid and other reagents.

Jacquelain discovered that the stable compound of sulphur trioxide and ammonia, his "sulphamide," is derived from, 2 mols. of the oxide and 3 mols. of ammonia.

Berglund determined the constitution of this stable compound to be imidosulphonic, by ascertaining that it behaves as an ordinary ammonium salt only to the extent of two-thirds of its nitrogen.

To Fremy is due the discovery that hydrolysis of the main product of the action of a nitrite upon a sulphite yields a salt, his "sulphamidate," now known to be an imidosulphonate; and that this salt exhibits the reactions which are neither those of a nitrite nor of a sulphite, and that it can be so far hydrolysed as to yield ammonia.

Fremy and, subsequently, Claus and Koch attributed to this salt a composition which was that of an addition compound of ammonia, but Berglund showed that this was incorrect, as he established the identity of Fremy's potassium sulphamidate, and Claus's "disulphammonate," with potassium imidosulphonate prepared from ammonium imidosulphonate obtained by the action of ammonia on chlorosulphonic acid. Mendeléeff (abstr. in *Ber.*, **3**, 872) had just before this suggested such a constitution as possibly belonging to Fremy's sulphamidates. In his *Principles of Chemistry* (1891), however, apparently unaware of Berglund's results, he treats parasulphatammon as being ammonium amidosulphonate. More recently, Raschig showed that the properties of Fremy's salts are inconsistent with Claus's view that they are compounds containing quinquevalent nitrogen.

Claus recognised the sulphonic constitution of these salts, whilst Berglund's discovery that they are formed by the mutual action both of sulphur trioxide and ammonia, and of sulphur dioxide and a nitrite, supplied an admirable confirmation of Claus's theory.

* Woronin's paper we only know from abstracts in the *Jahresbericht* and *Watts' Dictionary*. Berglund's memoir also, in the *Lunds universitäts Arskrift*, we have not seen.

Although, as we shall demonstrate, Rose, Jacquelain, Fremy, and Woronin had all prepared imidosulphonates with three equivalents of base, as well as those with two, to one of nitrogen, yet no clear conception of these compounds as salts of an acid higher than bibasic had been formed before they were examined by Berglund, who showed that they were derivatives of a tribasic acid, in which both the aminic, and the sulphonic, hydrogen is basic. He was the first to prepare the tripotassium and some other analogous salts.

It will be seen that the existence of imidosulphonates with three equivalents of base, first observed by Berglund, makes the term *imidosulphonate*, which he himself introduced, a misnomer, since in these salts all the hydrogen atoms in ammonia are displaced. As, however, no simple way out of this difficulty presents itself, we have adopted the name as Raschig and Mente had done previously.

Imidosulphonic Acid.

Imidosulphonic acid, $HN(SO_3H)_2$, first prepared by Jacquelain, has only been obtained in solution. We have employed his process, which consists in treating the lead salt, suspended in water, with hydrogen sulphide, using special care to have the lead salt as free as possible from sodium. It was decomposed by the hydrogen sulphide with very sensible elevation of temperature, and this strengthened our expectation that the acid must be hydrolysed almost as fast as it is formed; this, however, was found not to be the case, as, on filtering rapidly with the aid of a vacuum pump, it gave a concentrated solution containing very little sulphuric acid, and therefore very little amidosulphonic acid.

The imidosulphonic acid was fully identified by the abundant precipitate which it gave with excess of baryta-water being readily soluble in nitric acid, with the exception of a little sulphate; and particularly by its yielding an abundant crystalline precipitate with potassium acetate. Jacquelain converted his acid into the very soluble dibarium salt by just neutralising the acid with baryta, although he was aware that excess of baryta would give him the insoluble salt. On leaving the solution of the acid in a vacuum desiccator, we found that it became almost wholly hydrolysed to amidosulphonic acid in 18 hours or less.

Fremy attempted to prepare the acid by adding hydrofluosilicic acid to potassium imidosulphonate, but found that the acid decomposed almost immediately, the products of decomposition being sulphuric acid, sulphurous acid, and ammonia, but in this he must have erred. Berglund prepared the acid as Jacquelain had done, and found it very unstable.

We find that dry dipotassium imidosulphonate may be mixed with dry potassium hydrogen sulphate, and fused without being affected. At temperatures high enough, however, 420—450°, the imidosulphonate suffers the same decomposition as when heated alone. To prevent decomposition of the salts, moisture must be excluded, and we have therefore worked in a Sprengel-pump vacuum. When the fused mixture of the two salts is cooled, powdered, and treated with alcohol or ether, only a very little sulphuric acid passes into solution.

Dipotassium imidosulphonate, in dry, fine powder, mixed with 2 mols. of sulphuric acid of sp. gr. 1·84, forms a thin paste, which, if kept in a dry atmosphere, soon solidifies to a hard, somewhat translucent mass. This when powdered and exposed to air does not deliquesce, neither does it undergo any apparent change if left for days in dry air. On dissolving such a preparation in water to which a little potassium hydroxide has been added to guard against hydrolysis, it yields much unchanged imidosulphonate, together with amidosulphonate, but no ammonia. The presence of amidosulphonate is no doubt due to water taken up from the air during mixing, and from the sulphuric acid itself, and lastly, to some degree, during its dissolution in water, in spite of the alkali present. When heated, the mass very readily fuses and gives off sulphuric acid and sulphur dioxide. Jacquelain observed a similar behaviour with sulphuric acid, hot and cold, in diammonium imidosulphonate.

The comparatively slight action of concentrated sulphuric and nitric acids was noticed by Fremy, and by Claus and Koch. No evidence, therefore, has been obtained of any action of sulphuric acid on a dry imidosulphonate such as would be expressed by the equation

$$HN(SO_3K)_2 + 2SO_4H_2 = HN(SO_3H)_2 + 2HKSO_4.$$
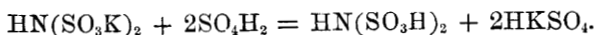
Ammonium Imidosulphonates.

Diammonium Imidosulphonate, $HN(SO_3NH_4)_2$.—The diammonium salt can be prepared from ammonia and sulphur trioxide (Rose, Jacquelain, Woronin), or chlorosulphonic acid (Berglund, Mente), or sulphuryl chloride or pyrosulphuryl chloride (Mente). It is obtained when nitrous gas is passed into an ice-cold solution of ammonium sulphite, and the product hydrolysed (Fremy). It is also formed together with ammonia on heating ammonium amidosulphonate to 160° (Berglund).

The decomposition of barium imidosulphonate by a solution of ammonium sulphate can only be very imperfectly accomplished, but by treating it first with dilute sulphuric acid in quantity barely sufficient to convert it into the soluble barium hydrogen salt (p. 965),

and then adding ammonium sulphate until the barium is completely precipitated, diammonium imidosulphonate can be prepared in a satisfactory manner. Another method is to decompose either of the hydroxy-lead imidosulphonates (p. 970, *et seq.*) with a solution of ammonium carbonate.

Triargentic imidosulphonate (p. 974), stirred with a solution containing the equivalent quantity of ammonium bromide, has been our source of the diammonium salt. The solution of triammonium salt thus produced is decanted from the silver bromide, evaporated on a water-bath until ammonia almost ceases to be given off, and filtered from a little silver bromide. To obtain the salt in a crystalline state, the solution generally requires further evaporation, but is kept alkaline by occasionally adding a drop of strong ammonia, so as to avoid hydrolysis into amidosulphonate during the operation.

Diammonium imidosulphonate forms monosymmetric prisms, isomorphous with the potassium salt (Münzing and Raschig). In its general reactions it is like the sodium and potassium salts. It reddens blue litmus even while still quite free from sulphuric acid (Jacquelain).

The effect of heating it was tried by Rose, and is described in the first of his papers on the "sulphatammons." According to him the products differ little from those obtained on heating ammonium sulphate, except that there is no water present. Ammonia and sulphur dioxide are evolved, first the former, then principally the latter. The residue consists of acid ammonium sulphate if the temperature is not too high. In the neck of the retort, ammonium sulphite and sulphate are found; in the receiver, the former salt only. He found that, when the salt is heated in gaseous ammonia, but little sulphate is formed.

This account given by Rose of the effect of heating diammonium imidosulphonate is essentially incomplete, but is true to the extent that ammonia, first, and then sulphur dioxide, are evolved, that these two partly condense as a sublimate, and that acid sulphate is formed. Heating in a roomy retort, and thus permitting the action of moist air, favours the change here described, and brings it still nearer to that caused by the action of heat on ammonium sulphate.

Jacquelain states that it is fusible without decomposition, and may be kept fused without change if heated in a current of dry ammonia, but that, a little above its melting point, it decomposes into ammonia, and ammonium sulphite, which sublimes, whilst a residue of ammonium hydrogen sulphate is left.
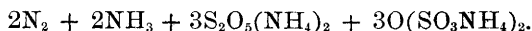
We are unable to confirm this. Diammonium imidosulphonate, which heated in a vacuum, suffers no change (except that it yields a very minute liquid sublimate at 190°) until very near to 357°, when

it melts and effervesces or boils. Most of the vapours condense as unchanged imodosulphonate just above the heated part of the tube, but a little ammonia is given off. At last, inconsiderable sublimates, white and yellow, appear some distance up the tube, consisting of compounds of ammonia with sulphur dioxide, and during their formation, minute quantities of nitrogen are liberated. On stopping the operation in an hour or two, when the evolution of gas is scarcely noticeable, the residue is found to be unchanged imidosulphonate mixed with a little acid sulphate. When the salt is subjected to a stronger heat, so as to be kept in violent ebullition, most of the unchanged salt condenses and flows back, and but little of it is got as a sublimate. On the other hand, there is more of the sulphite-ammonia sublimates, although they are still not abundant, and nitrogen is now given off more freely; the quantity, however, as well as that of the ammonia, is small, even if the heating is maintained for a long time. In one experiment, after about an hour's violent ebullition, the residue on being dissolved in sodium hydroxide solution in a closed vessel, and titrated with acid, was found to contain about one-fifth of its weight of ammonium pyrosulphate.

From what precedes it is evident that diammonium imidosulphonate is a comparatively stable compound, boiling and for the most part condensing unchanged. It, however, decomposes, but only very slowly, even when more strongly heated, into nitrogen ammonia, water, sulphur dioxide, and sulphur trioxide, thus :—

$$6HN(SO_3NH_4)_2 = 2N_2 + 14NH_3 + 6H_2O + 6SO_2 + 6SO_3,$$

these products then partly condensing, and yielding, finally,

$$2N_2 + 2NH_3 + 3S_2O_5(NH_4)_2 + 3O(SO_3NH_4)_2.$$

The ammonia first given off unmixed with nitrogen is no doubt attributable to the action of moisture in the somewhat deliquescent salt. This water would cause the hydrolysis of its molecular equivalent of the salt into amidosulphonate and acid sulphate, and then, by further heating, into pyrosulphate and ammonia :—

$$HN(SO_3NH_4)_2 + H_2O = H_2N \cdot SO_3NH_4 + HO \cdot SO_3NH_4 = H_3N + O(SO_3NH_4)_2.$$
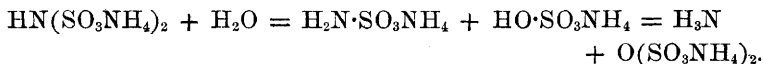
Experiments by one of us, as yet unpublished, have fully established the existence of the undescribed salt, ammonium pyrosulphate, $O(SO_3NH_4)_2$, referred to above.

Triammonium Imidosulphonate (hydrated).—This salt, hitherto undescribed, is formed by the union of ammonia with diammonium imidosulphonate in presence of water. The ammonia must be in excess, otherwise the salt is partly decomposed by water. The most

concentrated ammonia solution precipitates it from a saturated solution of the diammonium salt; also from a concentrated solution of the disodium salt, but in that case it is mixed with sodium ammonium salt (p. 961). Gaseous ammonia acts similarly and much more effectively. As thus obtained, it is a crystalline powder, but it can be got in large crystals by dissolving it, or the diammonium salt, to saturation in moderately strong ammonia, in a closed vessel by the aid of heat, and allowing the solution to cool. The largest crystals are prepared by evaporating its ammoniacal solution in a desiccator, over solid potassium hydroxide, and in a strongly ammoniacal atmosphere.

The crystals resemble those of the tripotassium salt, and are, therefore, asymmetric. They are clear and lustrous, but gradually effloresce (mostly through loss of ammonia), and become opaque and damp. The salt when dry smells faintly of ammonia, and its crystals in a dry ammoniacal atmosphere over solid potassium hydroxide very slowly become anhydrous and opaque throughout, while retaining much of their lustre and hardness.

When heated, the salt is converted mainly into the diammonium salt, but to some extent it melts, loses both ammonia and water, and hydrolyses into sulphate.

If dissolved in water, it decomposes, but very incompletely, into the diammonium salt and ammonia, and the solution when evaporated in the open air yields crystals of the diammonium salt only. Hence, when either the trisodium or the tripotassium salt is mixed with ammonium chloride, much ammonia is liberated.

It was analysed sufficiently by heating it to 160° very gradually in a current of dried air, in order to determine the water and third atom of ammonia. The sulphur was also estimated, and the salt was thus proved to have a composition analogous to that of the potassium salt, namely, $NH_4 \cdot N(SO_3NH_4)_2,OH_2$. The crystals, after rapid pressure in filter paper, were damp but transparent, and when analysed gave the following results:—

	Calculated.	Found.
Sulphur	26·0	25·4
Loss at 160°	14·2	16·0

Anhydrous Triammonium Imidosulphonate; "Sulphatammon."—Anhydrous triammonium imidosulphonate is, as we shall show, Rose's sulphatammon. Rose found that dry ammonia conducted into a flask lined with sulphur trioxide combines with the trioxide yielding two products, one a hard, vitreous matter, replacing the lining of sulphur trioxide, the other a loose, flocculent deposit.

Jacquelain got the same flocculent substance when he mixed vapour of sulphur trioxide with dry ammonia in excess. Rose found

that both the flocculent and vitreous matters when dissolved in water and evaporated yielded crystals of the same substance, but that the vitreous matter was often acid, through, as he considered, imperfect action of the ammonia. The crystals which he separated from the solution he called *parasulphatammon ;* they are now known to be diammonium imidosulphonate, and from what we ourselves have seen of sublimed diammonium imidosulphonate, we have very little doubt but that the vitreous matter is the same salt, and that the acid reaction occasionally observed is due to hydrolysis. From this it follows that the crystals are formed from three volumes of ammonia and two of sulphur trioxide, whilst Rose made out that they had the same composition as the undissolved flocculent matter, and were formed therefore from two volumes of ammonia and one of sulphur trioxide. He recognised, however, such differences in their properties that he held them to be distinct, and called the flocculent matter *sulphatammon.* Jacquelain prepared parasulphatammon from the flocculent matter by two methods, both without the use of water. He found it to be variable in composition, and one of his methods of getting crystalline pure parasulphatammon from it was to fuse it in a current of ammonia, allow it to solidify, and then stop the further entrance of ammonia before it cooled. His other method was to expose the flocculent matter, first, over sulphuric acid in a vacuum till it ceased to lose weight, and then to a moderate heat, which caused a further loss.

Having in a most careful manner proved that Rose's analysis of parasulphatammon was incorrect, Jacquelain himself no less strangely misconstrued the facts he had correctly observed. He found that parasulphatammon, prepared by the action of heat, if allowed to cool in contact with ammonia, absorbed it ; further that the flocculent matter, named sulphatammon by Rose, would lose from 6 to 9 per cent. of its weight in a vacuum over sulphuric acid, and the residue, if heated to 100°, gave up more ammonia, leaving parasulphatammon, as already mentioned. But he treated these phenomena as a case of the physical absorption of gases by porous solids, and likened the ammonia lost or taken up to hygroscopic moisture. Yet a compound of 2 mols. of sulphur trioxide with 4 mols. of ammonia has to lose as ammonia only $7\frac{1}{2}$ per cent. of its weight in order to become a compound of 2 mols. of sulphur trioxide with 3 of ammonia. As for the high loss of 9 per cent. recorded, that, if correctly observed, may have been due to loss of moisture, for, as Rose found, sulphatammon is markedly hygroscopic, and loses the moisture again at 100°.

Sixteen years later, Woronin first established the accuracy of Rose's analysis of the flocculent matter, sulphatammon, and then showed that this and parasulphatammon were different salts of the

same acid. Another 16 years later, Berglund claimed for sulphat-ammon that it must be triammonium imidosulphonate, since para-sulphatammon had proved to be diammonium imidosulphonate. But then, opposed to this conception of its nature there were the facts, first, that Rose had made no mention of its evolving ammonia when it was dissolved in water, and evaporated, so as to yield parasulphat-ammon ; secondly, that Raschig, much more recently, had dissolved an old specimen of parasulphatammon in ammonia solution, and on evaporation over sulphuric acid got only parasulphatammon again ; and, lastly, what is known to ourselves, at least, that trisodium, or tri-potassium, or triargentic imidosulphonate, when decomposed by ammo-nium chloride solution, sets free much ammonia. It seemed to us, therefore, at first to be as evident as it was probable that imido-sulphonic acid could not fix a third atom of ammonia along with its imidic hydrogen, and that Berglund's view might not be right.

Experiment has, however, established that sulphatammon is, as Berglund considered it, the triammonium salt. Crystals of the di-ammonium salt were coarsely ground (they are somewhat hygro-scopic, as just stated, and slip under the pestle, and so are not readily ground fine), and of this powder, a quantity equal to 2·29 grams if dried at 100°, was exposed to a current of carefully dried ammonia, of which it absorbed in two hours $5\frac{3}{4}$ per cent., and in two hours more another $\frac{1}{2}$ per cent., making altogether $6\frac{1}{4}$ per cent., the temperature being 20°; the calculated quantity is 8 per cent., but, considering the coarseness of the particles and the temperature, the result ob-tained may be regarded as satisfactory. The absorption of ammonia was attended with a very considerable change in the volume of the solid, and converted it into a bulky non-coherent, amorphous powder, the odour of which was only feebly ammoniacal. When dissolved in water, it became strongly ammoniacal, and the solution gave a copious precipitate with barium chloride, and otherwise behaved as a solution of the crystalline hydrated salt, which salt, indeed, it yielded when treated with gaseous ammonia. Evaporation of the solution gave crystals of the diammonium salt, which is just what Woronin observed with sulphatammon, the latter being converted into parasulphatammon.

On exposing it in a desiccator over sulphuric acid for three days at a temperature of about 20°, we found that it lost only about $\frac{1}{2}$ per cent. of its weight, so that probably the pure dry salt loses am-monia only in a damp atmosphere, although indeed Jacquelain has found sulphatammon (probably damp) sometimes give up much ammonia in a vacuum over sulphuric acid. Having observed the loss of ammonia to be so slight at the ordinary temperature, we heated the same portion in a current of well-dried air for $1\frac{3}{4}$ hours at a tem-

perature of 100—120°, and then found that the issuing air still con-
tained ammonia. The salt cooled and reweighed had lost only 5·4 per
cent. in weight during this heating, and when dissolved in water and
tested showed that some triammonium salt was still present.

From what precedes, it is evident that triammonium imidosulphon-
ate is comparatively stable in the anhydrous state, and that Rose's
sulphatammon is this salt.   Formed, as here described, from another
imidosulphonate without hydrolysis, it cannot be ammonium amido-
sulphonate, as it is commonly assumed to be (as in Mendeléeff's
Principles of Chemistry and Ramsay's *System of Inorganic Chemistry*).
Further, its conversion by heat into parasulphatammon and ammonia
affords no proof that it is ammonium amidosulphonate, for the latter
would only be changed at temperatures above 160°.   A salt which is
certainly ammonium amidosulphonate can be prepared by processes
which include the hydrolysis of an imidosulphonate, but it is quite
a different substance.   According to Berglund, it crystallises in large
plates, and is not converted into imidosulphonate and ammonia unless
it is heated at 160°.   It is not readily decomposed by water, is neutral
in reaction, and does not precipitate barium salts, facts verified for us
by Mr. Y. Osaka.

Imidosulphonamide, $HN(SO_2 \cdot NH_2)_2$.—Mente finds that this com-
pound is produced by the action of ammonia upon pyrosulphuryl
chloride.   Diammonium imidosulphonate, when heated to its sublim-
ing point, may possibly yield it, but as at ordinary temperatures it
reacts at once with water to form diammonium imidosulphonate, its
presence cannot be tested for.

Potassium Imidosulphonates.

Dipotassium Imidosulphonate.—This salt was obtained by Fremy by
the hydrolysis of potassium nitrilosulphonate, formed by the action of
sulphite upon nitrite.   Claus and Raschig have both published
accounts of the preparation of the salt in this way.   It has also been
obtained by double decomposition from diammonium imidosulphonate
and a potassium salt (Fremy, Berglund) ; also by Woronin from the
diammonium salt by converting it into Jacquelain's barium salt and
decomposing that with potassium sulphate.

Imidosulphonates may be readily enough prepared from nitrilo-
sulphonates by hydrolysis, but as the two potassium salts are only
sparingly soluble in water, and the imide salt very readily passes into
the amide salt by further hydrolysis, the method of preparation of
dipotassium imidosulphonate hitherto employed gives very uncertain
results.   On the other hand, the conversion of sodium nitrilosulphon-
ate into disodium imidosulphonate can be effected very easily and

completely; and as the disodium imidosulphonate is very soluble, the insoluble potassium salt can be prepared from it by double decomposition without any trouble. Prepared in this way, it is very pure, and consequently stable. It can also be recovered from mercuric dipotassium imidosulphonate by the action of nitric acid (p. 977).

Dipotassium imidosulphonate is also formed when potassium amidosulphonate is heated. Our earliest knowledge of this interesting change—$2H_2NSO_3K = H_3N + HN(SO_3K)_2$—is due to Berglund. We ourselves find that at or just below $350°$ this change takes place readily, the gas evolved being ammonia, and free from nitrogen. At this temperature, the salt fused, and then gradually solidified as the decomposition proceeded; the salt we used was not pure, however, being mixed with potassium sulphate.

The effect of heat on dipotassium imidosulphonate has also been studied by us. Below the softening point of soft lime-glass, the dry dipotassium salt in a dry atmosphere does not undergo any notable change, but in a Sprengel vacuum, it evolves gas, although very slowly and of very low tension, and yields a very slight sublimate between $360°$ and $440°$. At the temperature of actual decomposition, it melts and boils, the change which occurs being expressed by the equation

$$3HN(SO_3K)_2 = N_2 + NH_3 + 3SO_2 + 3K_2SO_4.$$

The ammonia and some of the sulphur dioxide unite to form a rather volatile, yellowish-brown sublimate, and a less volatile, white sublimate, both of which readily give the reactions for ammonia and sulphur dioxide when dissolved in water. The brown sublimate gives a clear, colourless solution. Both sublimates appear to have been obtained by Rose from sulphur dioxide and ammonia. Probably, judging from Mente's researches, the yellow compound is nitrogen sulphide, and the white is sulphamide. The permanent gases consist of one volume of nitrogen to somewhat more than two of sulphur dioxide. We had expected to be able to get evidence of the intermediate formation of nitrilosulphonate—$3HN(SO_3K)_2 = H_3N + 2N(SO_3K)_3$—by arresting the decomposition before it had gone very far, and by carefully regulating the temperature, but we were as unsuccessful as in the case of the diammonium salt.

Fremy observed that the action of heat gave rise to potassium sulphate, sulphur dioxide, ammonia, and a coloured sublimate. Claus and Koch recorded the decomposition of the salt above $200°$ sharply with the same results. But neither chemist mentions the still more abundant white sublimate, and, what is of more significance, the nitrogen; had they done so, it would have been seen that the salt is not an addition compound of ammonia, as they supposed.

One of the remarkable properties possessed by imidosulphonates, as well as by oximidosulphonates, is that of hydrolysing at a sufficiently high temperature by fixing the moisture of the air. Claus had observed slow increase in weight of potassium nitrilosulphonate and of oximidosulphonate (his trisulphammonate and disulphydroxyazate) when they were heated in the air, but wrongly ascribed this increase to oxidation. Oxidation it could not be, for this would only give rise to volatile products, such as water, or oxide of nitrogen, or nitrogen itself, and not increase the weight of the fixed matter. We have, besides, fully proved by experiment that at the temperature at which any imidosulphonate increases in weight in ordinary air, or even at a higher one, that salt remains for hours unchanged in weight and appearance if the air is dried, and yet if the air is undried it begins to increase in weight. The product of hydrolysis produced by the moisture in ordinary air causes the imidosulphonate to lose its crystalline lustre, cake together, and become acid. In order to prevent hydrolysis of those imidosulphonates which, like the disodium salts, contain water of crystallisation, it is necessary to dry them slowly at a gradually rising temperature, and even then it is difficult to dehydrate them. Dipotassium imidosulphonate, the crystals of which are anhydrous, is particularly stable, and may be heated for hours at 140° or higher in undried air without the least sensible change; at 170—180°, however, it slowly fixes water and hydrolyses.

As the tripotassium imidosulphonate is much more soluble than the dipotassium salt, the latter dissolves readily in potassium hydroxide solution, from which it can be precipitated by carbonic acid (Raschig). Other and new reactions of the dipotassium salt observed by us are so similar to those we record of the sodium salt as to render it unnecessary to give them in detail.

Tripotassium Imidosulphonate.—Tripotassium imidosulphonate was prepared by Berglund, and again by Raschig, by dissolving the dipotassium salt in a solution of potassium hydroxide, evaporating, and crystallising.
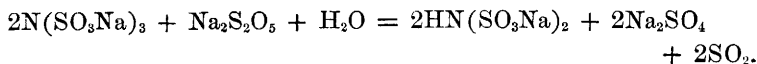
Sodium Imidosulphonates.

Disodium Imidosulphonate.—Fremy's method for the preparation of the potassium salt is employed, but the details of working differ materially. Sodium nitrite as nearly pure as possible and sodium carbonate in crystals, in the proportion of 2 mols. of nitrite to 3 mols. (6 equivalents) of carbonate, mixed with twice their weight or more of water, are treated freely with sulphur dioxide in a capacious flask fitted with cork and gas tubes. After the carbonate crystals have dissolved, and the hydrogen carbonate precipitated and redis-

solved with continuous effervescence, the liquid, still quite alkaline to litmus, begins to grow warm, as it continues to absorb sulphur dioxide. To prevent any considerable rise of temperature, which might cause premature hydrolysis and spoil the operation, the flask is now kept cool by agitating in cold water, and the stream of sulphur dioxide some-what moderated and carefully controlled. Neutralisation of the alka-line liquor by the sulphur dioxide is markedly retarded by the action of the nitrite, in the presence of which neutral sulphite cannot exist. When at length neutrality to lacmoïd paper is almost reached, the flask is actively agitated without intermission, the flow of gas greatly diminished, and then at once stopped, when the paper is just perma-nently reddened. The solution at this stage contains, besides a very little sulphate, nothing but the two salts nitrilosulphonate and meta-sulphite, which, omitting notice of intermediate stages, have been formed as follows :—

$$2NaNO_2 + 3Na_2CO_3 + 8SO_2 = 2N(SO_3Na)_3 + Na_2S_2O_5 + 3CO_2.$$
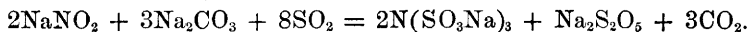
The apparently redundant metasulphite is necessary in order to get the nitrite converted wholly into nitrile salt. Its presence is almost equally essential for the preservation of the imidosulphonate about to be formed.

When complete neutrality is reached, or, perhaps, just passed, the solution, after a few minutes, suddenly becomes strongly acid and warm, and evolves much sulphur dioxide. Hydrolysis has occurred, but, owing to the presence of the metasulphite only through one stage, and the liquid now contains nothing but imidosulphonate, sulphate, and sulphur dioxide—

$$2N(SO_3Na)_3 + Na_2S_2O_5 + H_2O = 2HN(SO_3Na)_2 + 2Na_2SO_4 + 2SO_2.$$

Sulphurous acid appears to have no immediate hydrolysing action upon the imidosulphonate, but, as it would become oxidised to sulph-uric acid, it must be removed. A rapid current of air is, therefore, passed through the liquid for half an hour or so, after which the addition of a very little sodium carbonate suffices to render it slightly alkaline and quite stable. It is now evaporated on the water-bath, so far as necessary, and then cooled to 0°, or a little below, when, in the course of some hours, most of the sulphate crystallises out. A second evaporation and cooling is generally needed to separate more of the sulphate, after which further evaporation and cooling to the ordinary temperature causes the separation of the disodium imido-sulphonate in well-formed crystals. The mother liquor can be further worked for sulphate and imidosulphonate, if worth the trouble.

3 x 2

The reaction proves to be almost quantitative, for the salt obtained in crystals is 80 per cent., whilst there is considerable loss of salt in the mother liquors adhering to the very voluminous masses of sodium sulphate.   The crude salt can be purified by recrystallisation from warm water, rendered slightly alkaline as a precaution against hydrolysis.

Instead of sodium carbonate, the equivalent quantity of normal sulphite, or of metasulphite, pure, and therefore freshly prepared, may be used along with the additional sulphur dioxide indicated by the equation already given.   The mixture of nitrite and metasulphite becomes at once alkaline and rapidly heats up, so as to need cooling, in accordance with what has been stated.   This mode of procedure is certainly less simple and less practicable than that described.   It may also be mentioned that a sufficient excess of metasulphite will of itself convert all the nitrite to nitrile salt, but as, in that case, the addition of another acid is required to effect hydrolysis, the process does not give a good yield of imidosulphonate crystals.
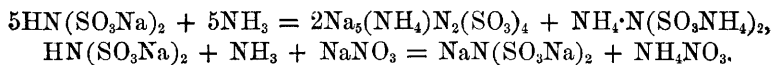
It is not unfrequently convenient to prepare disodium imidosulphonate from the trisodium salt.   The latter can be preserved without any special precautions, which is not the case with the disodium salt. Again, where the direct process for preparing sodium imidosulphonate has been carried out with impure salts, or if the proportions to be used, and other details, have not been rigidly adhered to, it may not be so easy to crystallise out the disodium salt, and here the very ready separation and purification of the trisodium salt becomes advantageous.   From the trisodium salt, the disodium imidosulphonate can be prepared by treating the crystals with sulphuric acid slightly diluted, until neutrality to litmus is reached.   The solution, with any crystalline precipitate (sulphate), is kept for some hours at or about $0°$, and the mother liquor decanted, while still at that temperature, from the sodium sulphate.   Evaporation, as already described, then yields the disodium salt in good crystals, pure, or almost so.

Disodium imidosulphonate crystallises readily in large, rhombic prisms.   It is very soluble in water, slightly acid in reaction, and devoid of sulphurous taste.   Its crystals, which contain water, do not effloresce, even in dry seasons, so that crystals of sodium sulphate among them may be easily recognised.   In air kept dry by sulphuric acid, they slowly become opaque, but retain their shape, along with much of their lustre and hardness, whilst the rate of loss, even when they have been crushed, is so slow as to make a water estimation in this way almost impracticable.   They can generally be kept for many weeks in bottles, and apparently for any time in a sufficiently dry atmosphere, but are liable to undergo hydrolysis into an acid mixture

of sulphate and amidosulphonate. The solution of the salt is also unstable, but it may be heated for a short time to a moderate degree without change. The crystals can hardly be heated to $100°$ without some decomposition.

The decomposition of disodium imidosulphonate, which almost unavoidably attends the removal of the water of crystallisation, also complicates observation of the effects of a high temperature on it. For having been to some extent converted by this water into sulphate and amidosulphonate, it gives at first, when heated, only ammonia, coming from the reconversion of the amidosulphonate into imidosulphonate. But, at a higher temperature, this is followed by products the same as in the case of the dipotassium salt, namely, nitrogen with more than double its volume of sulphur dioxide, small brown and white sublimates, and sodium sulphate. The sodium salt appears to be much more fusible than the potassium salt, but then the latter was practically pure, whilst the former was mixed with the products of its hydrolysis, which must have affected its fusibility.

Disodium imidosulphonate in aqueous solution, like the far less soluble dipotassium salt (Berglund), does not give a precipitate with many of the usual metal salts. In moderately concentrated solution, however, it gives a precipitate of dipotassium imidosulphonate with solutions of potassium salts; of trisodium imidosulphonate with sodium hydroxide; and of a barium sodium imidosulphonate with barium hydroxide; concentrated ammonia solution also gives an abundant precipitate, which, when the disodium imidosulphonate is unmixed with other salts, consists of a sodium ammonium salt (p. 961); if, however, a little sodium nitrate, chloride, or other sodium salt is added before the ammonia, the latter, in concentrated solution, precipitates pure trisodium imidosulphonate. The two forms of precipitation are expressed by the respective equations:—

$$5HN(SO_3Na)_2 + 5NH_3 = 2Na_5(NH_4)N_2(SO_3)_4 + NH_4 \cdot N(SO_3NH_4)_2,$$
$$HN(SO_3Na)_2 + NH_3 + NaNO_3 = NaN(SO_3Na)_2 + NH_4NO_3.$$

The precipitation by ammonia is in both cases greatly increased by excess of the reagent, and if the disodium imidosulphonate is added in powder to strong ammonia, much of the triammonium salt also precipitates.

Hydroxy-lead acetates, as was known, give copious precipitates. Normal lead acetate also gives a scanty precipitate of a lead imidosulphonate, even when the acetate is truly normal and the disodium salt in solution faintly acid to litmus (p. 969). Lead nitrate occasions no precipitate, but, unlike the acetate, it rapidly effects hydrolysis, and consequently precipitation of a little lead sulphate takes place.

Both mercury nitrates are also precipitating agents, acting here as they do when added in excess to a solution of trisodium imidosulph-onate (p. 960). Mercuric oxide, especially the precipitated form, reacts with it to give mercuric disodium imidosulphonate (p. 980). Warmed with a moderately concentrated solution of the salt, the mercuric oxide dissolves, and, on cooling and standing, it deposits crystals of the double salt. Silver hydroxide is rapidly converted, by solution of disodium imidosulphonate, into the sparingly soluble silver disodium salt (p. 976). Cupric hydroxide is without action.

Evaporated on the water-bath with sodium carbonate, or even with the acetate, disodium imidosulphonate is partly converted into tri-sodium imidosulphonate, whilst carbon dioxide or acetic acid escapes. When acetate is used, therefore, there is the striking phenomenon of a strongly acid vapour rising from a liquid having a well-marked alkaline reaction.

In analysing the salt, we hydrolysed it by heating it with hydro-chloric acid at 150° in sealed tubes for some hours, following Raschig's process for the analysis of the potassium salts. The composition of the salt is expressed by the formula $HN(SO_3Na)_2,2H_2O$, the results of analysis being—

	Calculated.	I.	II.	III.	IV.
Sodium	17·90	17·17	17·76	—	—
Sulphur....	24·90	—	—	24·88	24·78
Nitrogen ...	5·45	—	—	5·40	—

Trisodium Imidosulphonate.—This is prepared from the disodium salt by adding sodium hydroxide to its strong solution. It is un-necessary to have the disodium salt pure and in crystals. After following the process for getting this salt so far as to separate one good crop of sodium sulphate crystals, the solution is diluted with twice its volume, or more, of water, sodium hydroxide solution added, till it tastes slightly caustic, and then cooled in an ice-box. The trisodium salt begins to separate almost immediately after the addi-tion of the sodium hydroxide, but the water previously added retards the separation, and allows the crystals to grow in the cooled liquid; in this way they can be better freed from the mother liquor. When collected and pressed on calico, the salt is almost pure, and can be rendered fully so by recrystallisation.

Trisodium imidosulphonate is easily prepared, and is a very stable salt. It forms thin, overlapping, hexagonal plates, which may grow to considerable size, but are seldom, if ever, to be seen single and perfect, or of very great thickness. The crystals readily effloresce in

dry air, and have a mildly alkaline taste. The salt is sparingly soluble in very cold water, but very soluble in hot water, taking for dissolution at 27·5° about 5·4 parts of water. Its solution readily shows supersaturation. It is alkaline to litmus, and even to phenol-phthaleïn, but has no action whatever on iodine solution; it is pre-cipitated from its aqueous solution by alcohol without decomposition, and can be repeatedly recrystallised without any loss of alkali. Aqueous solutions are quite stable, even when boiled for a long time. The crystals melt when gently heated, and their water may be rapidly boiled off without causing any decomposition of the salt. In a vacuum over sulphuric acid, they lose only 11 mols. H_2O out of the 12 they contain. The salt loses more water when heated, but even at 160° it retains some, possibly through hydrolysis, so that, heated until decomposition begins, it always yields a very little water and ammonia (gas and sublimate). Heated in a vacuum, however, it yields even still less, so that atmospheric moisture seems to be active in hydrolysing it when heated in air.

The presence of hydrogen in the dried salt might have particular significance, since Fremy, and after him Claus, have represented the dipotassium salt as containing three atoms of hydrogen instead of the one given by the imide constitution and displaced by the metal in the normal salts. But careful combustion of some grams of the dried salt with copper oxide gave us in one case only 0·22 per cent., and in another only 0·24 per cent. of water, calculated from the hydrated crystals, and such a percentage corresponds to only about one-ninth of an atom, instead of the extra two, of hydrogen required by the sulphammonate constitution given by Claus.

When dried trisodium imidosulphonate is heated somewhat strongly in an open tube, it melts and effervesces, yields nitrogen and some sulphur dioxide, and sulphur which sublimes. The saline mass becomes also very dark coloured, from the presence in it of sulphur, and gradually solidifies, until at an incipient red heat it forms a semi-fused *hepar sulphuris*. By heating in a vacuum, proof is ob-tained that the sulphur dioxide comes only from the action of the air upon the sulphur. From 350° to 440°, gas of only very low tension is given off, along with sulphur vapour, forming a sublimate of drops. Just below the softening point of good soft lime-glass, the salt fuses and effervesces. The gas consists entirely of nitrogen. Some of the sulphur remains in the fused mass, partly free, partly as thiosulphate. A trace of sublimate of the ammonia compound with sulphur dioxide is formed. Apart from this, the reaction is expressed by the equation

$$2NaN(SO_3Na)_2 = N_2 + S + 3Na_2SO_4.$$

Acids readily dissolve trisodium imidosulphonate, yielding neutral solutions of the disodium salt when the quantity of acid is equivalent to one-third of the sodium. The action of concentrated sulphuric acid is remarkable ; if it is not in excess, it dissolves the crystals, with marked fall of temperature, although if the quantity present is more than enough to form the disodium salt, heat is developed. From the neutralised solution, sulphate and disodium imidosulphonate can be crystallised out. Carbon dioxide also decomposes the trisodium salt in aqueous solution, sodium hydrogen carbonate being precipitated if the amount of water present is not too great. Concentrated ammonia precipitates the trisodium salt free from ammonia, and with its usual water of crystallisation. Ammonium salts suffer double decomposition with the trisodium salt, ammonia then becoming free by the decomposing action of water upon some of the triammonium salt. When concentrated solutions of the trisodium salt and of a potassium salt, such as the nitrate, are mixed, no change is observable, but on neutralising with an acid, the dipotassium salt is precipitated in crystals.

Trisodium imidosulphonate, unlike the disodium salt, precipitates many metallic salts, giving in some cases, however, only hydroxides. Precipitates of imidosulphonates are obtained with silver nitrate, the mercury nitrates, lead salts, and barium salts, whilst with calcium chloride crystals may slowly form which are of characteristic appearance. Specially noteworthy is the fact that silver nitrate added in different proportions yields three precipitates, distinct both in appearance and in composition. The compounds formed by these reagents are described later in this paper. Mercuric chloride has apparently no action upon trisodium imidosulphonate, for nothing separates, and the reaction to litmus remains alkaline. Mercuric oxide dissolves to a limited extent in solutions of the trisodium salt, more being dissolved in proportion to the trisodium salt, the weaker these solutions are ; it makes them somewhat caustic (see in this connection, the reaction of mercuric disodium imidosulphonate with alkali hydroxide, p. 982).

It was not practicable to get the crystals of trisodium imidosulph-

	Calculated.	Found.		
		I.	II.	
Moisture..	$1\cdot00$ ⎱	$43\cdot66$	$43\cdot56$	Loss *in vacuo.*
11 mols...	$42\cdot70$ ⎰			
1 mol. ..	$3\cdot88$	⎰ $3\cdot71$	$3\cdot64$	Loss at $110°$.
		⎱ $(0\cdot23$	$0\cdot27$	Retd. at $110°$).
Total	$47\cdot59$	$47\cdot60$	$47\cdot47$	

onate completely dry for analysis, because the thin plates adhering together retained mother liquor, and, on the other hand, during much crushing and pressing with paper they effloresced. Avoiding the latter source of error, our results were $12\frac{1}{4}H_2O$, the $\frac{1}{4}$ representing 1 per cent. of moisture. The numerical details of the water determinations, which are a little complex, are given in the table, p. 960.

We have already given (p. 959) the percentage of retained water, as actually found in the salt dried with special care, as 0·22 and 0·24 per cent. The above numbers, 0·23 and 0·27, are difference numbers.

The analysis of the dried salt gave—

	Calculated.	Found.
Sodium	28·40	28·24
Sulphur	26·34	26·46
Nitrogen	5·76	5·92

The formula of the salt is therefore $NaN(SO_3Na)_2,H_2O + 11H_2O$.

Sodium Ammonium Imidosulphonate.

Possibly a salt two-thirds sodium and one-third imidosulphonate might be got in presence of an excess of the triammonium salt, but this is doubtful, because of the sparing solubility of the following salt in presence of ammonia, and because ammonia and another sodium salt convert disodium into trisodium imidosulphonate.

Pentasodium Ammonium Imidosulphonate.—This salt crystallises from dilute solution with 7 mols. H_2O, $Na_5AmN_2(SO_3)_4,7H_2O$, but from concentrated saline solution it crystallises with less water. To prepare the fully hydrated salt, strong ammonia solution is added in large excess to a solution of disodium imidosulphonate, which must be free from sulphate or other salt. Separation of the salt begins at once, or very soon, and continues for some time if the liquid is kept nearly ice-cold. It forms minute prisms, which bear moderate washing with concentrated ammonia, and can be drained on a tile, unchanged if under close cover. When dry, the salt does not smell noticeably of ammonia. The numbers obtained by calculation and experiment are as follows :—

	Calculated.	Found.
Sodium	18·95	19·19
Ammonium	2·97	2·85
Sulphur	21·09	20·95

A salt with $2\frac{1}{2}$ mols. H_2O only falls as a crystalline precipitate on adding strong ammonia to a solution of trisodium imidosulphonate and its equivalent at least of ammonium nitrate (3 mols.). Being but

very little soluble in ammonia solution, it can be properly washed
with this, and may then be drained on a tile under cover, without
change.   When heated, it loses water and ammonia without suffering
aqueous fusion.   It contains no nitrate.   Analysis gave—

	Calculated.	Found.
Sodium	21·86	22·01
Ammonium	3·42	3·40
Sulphur	24·34	24·40

For notice of a monohydrogen sodium ammonium imidosulphonate,
one in which the ammonium greatly predominates over the sodium,
see p. 963.

Hydrogen Sodium Ammonium Imidosulphonate Nitrate.

On dissolving trisodium imidosulphonate and then its equivalent of
ammonium nitrate (3 mols.) in half their combined weight of hot
water in a closed, nearly full vessel, a cold solution is obtained, which
sometimes remains supersaturated and unchanged, sometimes slowly
deposits the trisodium salt of the ordinary form, but in thicker
crystals.   The attempt to redissolve the crystals by dipping the vessel
in hot water readily succeeds, but is generally attended with the
copious separation of some white opaque salt (sodium ammonium
imidosulphonate ?).   On the vessel being left for some days in a cold
place with occasional agitation, the trisodium salt re-forms in crystals,
and the opaque salt redissolves.   When, however, the fresh mixed
solution of the trisodium salt and ammonium nitrate in half their
weight of water is placed in the steam-bath in an open glass capsule,
ammonia freely escapes, and soon, groups of small prisms form,
evidently in consequence of the loss of ammonia by the solution, and
not its mere evaporation, for the addition of some water has little
effect on the quantity of these crystals.   The crystals could not be
separated from their highly-concentrated mother liquor in a state
fit for trustworthy analysis, but we are pretty confident of their being
the salt now to be described.

A well-crystallised double salt of definite composition is obtainable
bv evaporating a solution of trisodium imidosulphonate with at least
its equivalent of ammonium nitrate until the liquid is nearly neutral,
then adding water to redissolve any crystals which have formed, and
leaving the product to cool slowly.   Throughout, care must be taken
that the solution does not become acid during evaporation ; this can
be prevented by adding a drop or two of ammonia when necessary.
In this way small, flat, thick prisms are obtained which are anhydr-
ous and stable in the air.   They cannot be washed, and must be

freed from their mother liquor by pressure in paper. The composition of the new salt may be represented as being that of 1 mol. of diammonium imidosulphonate with 1 mol. of sodium nitrate. If a good excess of ammonium nitrate has been used, the crystals are almost pure, but hold a little water (a); with the use of less ammonium nitrate, the salt showed, on analysis, the presence of a very slight excess of disodium imidosulphonate. The yield of salt was three-fourths of the possible quantity. The mother liquor, on evaporation, gave crystals of sodium nitrate and some more of the salt. The double salt cannot be recrystallised, its solution yielding first good crystals of a salt which may be described as (anhydrous) diammonium imidosulphonate containing 3 per cent. of sodium, and, after this, crystals of the double salt. Since the mother liquor of the double salt yields sodium nitrate, it would seem that double decomposition occurs between sodium imidosulphonate and ammonium nitrate.

The presence of nitrate in the double salt cannot be directly indicated in the ordinary way, but may be at once detected by a new reaction of delicacy and of some general interest. The salt freely effervesces when immersed in strong sulphuric acid, the gas being nitrous oxide with a little nitrogen. No nitrosyl sulphate is produced. A very minute quantity of nitrate mixed or combined with an imidosulphonate can be detected by dropping the dry solid into a little of the acid, and not mixing them up too much. The reaction needs careful study. We ventured to determine the nitric acid in the salt by means of this reaction, taking the gas as nitrous oxide only, and got a good result, but do not feel justified in entering it in the tabular statement below.

In one preparation we determined the nitric acid; in the other it was undetermined, except in the experiment above referred to. The nitric acid was estimated by evaporating the salt with barium hydroxide to expel ammonia, filtering off the barium imidosulphonate, removing barium as carbonate, and then putting the concentrated solution of sodium nitrate into the nitrometer. The result was low, but that is hardly to be wondered at. Water, in that preparation in which it was present in any quantity, was estimated by heating the salt in dried air, and the result can be only approximate, for slight hydrolysis, with fixation of water, is hardly to be avoided.

	Calculated.	a.	b.
Sodium..............	7·77	8·00	8·42
Ammonium	12·16	11·71	11·37
Sulphur	21·62	21·62	22·08
Hydrogen nitrate	21·28	19·93	—

The preparation *a* was formed in presence of a good excess of ammonium nitrate, and *b* in presence of little more than enough of it. The calculation is for $HN(SO_3NH_4)_2,NaNO_3$.

Hydrogen Sodium Potassium Imidosulphonate Nitrate.

The very sparingly soluble dipotassium imidosulphonate is hardly affected by digestion with a cold dilute solution of sodium nitrate, and when dissolved in it by heating crystallises out again almost unchanged; if, however, it is left in a concentrated solution of sodium nitrate, it removes this salt from it. Taking about equivalent quantities of the salt, $HN(SO_3K)_2 : 3NaNO_3$, and leaving the solution of the nitrate standing over the powdery dipotassium imidosulponate in a loosely-covered beaker for some days, the latter gives place to a caked mass of crystalline granules, apparently homogeneous when seen under the microscope, but with no well-defined forms. The decanted mother liquor, evaporated a little, gives more of the granules, but no crystals of sodium or potassium nitrate. The granular mass, drained and pressed on a tile, has a composition closely approaching that of 1 mol. of dipotassium imidosulphonate to 1 mol. of nitrate, the potassium and sodium nitrates being in molecular proportion, $NaNO_3,KNO_3,2HN(SO_3K)_2$. It is decomposed by water, and is anhydrous.

	Calculated.	Found.
Sodium	3·32	3·61
Potassium	28·23	27·34
Sulphur	18·48	18·89
Hydrogen nitrate	18·20	18·01

The two potassium salts or the two sodium salts do not form double salts together. Disodium imidosulphonate and potassium nitrate suffer double decomposition. The formula of the salt just described shows also that, to some extent this double decomposition is reversible.

In our next communication we shall have to describe still more remarkable combinations of nitrates with oximidosulphonates.

Barium Imidosulphonates, Simple and Double.

Barium Imidosulphonate.—This salt has been prepared by Berglund, but no particulars of it have been published, except possibly in Swedish. It is obtained as a voluminous, coherent precipitate when trisodium imidosulphonate is added gradually to a solution of barium chloride kept in excess. When drained on a porous tile, after

thorough washing, it is still very bulky, and hangs together in soft
flocks, more like some organic salt than an inorganic barium salt. It
retains moisture in the interstices of the matted masses of crystals
with remarkable obstinacy, so that it cannot be made dry by draining
on a porous tile or even in the desiccator except at the surface of
these masses; yet it is not in the least deliquescent, and becomes dry
in the air when spread out in very thin layers; indeed, in very
dry air it is even slightly efflorescent. Analysis shows that it con-
tains water, which it loses only very slowly even at 115°. Under the
microscope, it is seen to consist of very long, slender, interlacing
needles. It is only very slightly soluble in water, merely enough to
cause the water to give a very slight opalescence with sulphuric acid.
It is alkaline to litmus. It is decomposed a little by solutions of alkali
carbonates. It may be dissolved in dilute nitric acid, and, with very
rapid treatment, reprecipitated unchanged by barium hydroxide.
This is a property which, with' precautions, may be taken advantage
of to remove sodium salt, which is nearly always present in the
original precipitate, but always absent after second precipitation.
Only once did we get the original precipitate free from sodium.

Analysis gave—

	Calculated.	Found.
Barium	48·38	47·91
Sulphur.	15·08	15·04
Nitrogen	3·29	3·31

The calculation is for $Ba_3N_2(SO_3)_4,5H_2O$. The alkalinity of the
salt, measured by decinormal acid and methyl-orange, proved equal to
one-third of the barium.

Ammonia added to a solution of the salt next described converts
it into the insoluble tribarium imidosulphonate and ammonium
imidosulphonate.

Barium Hydrogen Imidosulphonate.—This salt has been briefly
noticed by Jacquelain and by Berglund. We have prepared it from
the tribarium salt, entirely free from sodium, by cautious treatment
with dilute sulphuric acid equivalent to slightly less than one-third of
the barium, filtering off the barium sulphate formed, and evaporating
in a desiccator, when minute, brilliant, orthorhombic crystals are ob-
tained, moderately soluble in water. The salt is stable in the desic-
cator, or in the open air in dry weather, but soon hydrolyses in a
bottle. In dried air, it is stable even when heated considerably, but
it hydrolyses in ordinary air at 140°. Rapidly heated, it decomposes
suddenly, giving a cloud of barium sulphate. Its solution is acid to
litmus, but neutral to methyl-orange.

Proceeding in almost the same way as that followed by us

Woronin obtained apparently the same salt, but he assigned to it a molecule of ammonia more, calling it *barium sulphamate*. Since our preparation contains 1 mol. H_2O, the determination of barium and of sulphur agrees with both formulæ, $Ba(H_2NSO_3)_2$, "sulphamate," and $BaHN(SO_3)_2,H_2O$, imidosulphonate.

Quantitative analysis and the properties of the salt agree with the formula $BaHN(SO_3)_2,H_2O$.

	Calculated.	Found. I.	II.
Barium..........	41·51	41·67	41·65
Sulphur..........	19·39	19·51	—

In warm solution, barium hydrogen imidosulphonate reacts with mercuric oxide to form the double salt.

Barium Ammonium Imidosulphonate.—By adding 1 mol. of barium hydroxide to 1 mol. of triammonium imidosulphonate ("neutral ammonium sulphamate"), Woronin observed the formation of a "soluble" barium salt with evolution of ammonia; he made no statement as to its composition. On adding barium hydroxide gradually to triammonium imidosulphonate until it nearly ceased to give a precipitate, we obtained a very sparingly soluble salt, which was found to be barium ammonium imidosulphonate. It was not fully analysed, but gave a percentage of barium of 41·87, whilst calculation for $BaNH_4N(SO_3)_2$ requires 41·64 per cent. But it is not improbable from what follows that it may have been a hydrous salt with less ammonia.

The experiment repeated with diammonium imidosulphonate gave us a precipitate at first gelatinous, but becoming granular after a time. Under the microscope, it was seen to consist of granular crystals intermixed with a very few slender needles of the tribarium imidosulphonate, insignificant in amount. Its alkalinity, determined by decinormal acid and methyl-orange, showed it to be a normal salt, the alkalinity being equal to one atom of univalent base to two atoms of sulphur present. After hydrolysis, the total ammonia, as well as the sulphuric acid, was estimated. The results agree with the calculation for $Ba_5(NH_4)_2N_4(SO_3)_8,8H_2O$, a five-sixths barium salt, corresponding, therefore, to the sodium ammonium salt.

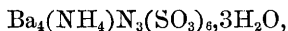|	Calculated.	Found.
Barium	43·88	43·84
Sulphur............	16·40	16·53
Nitrogen	5·38	5·27

It is here assumed that the observed presence of a very little of the tribarium salt could be disregarded. The assumption that the prepara-

tion was the mixture $Ba_3N_2(SO_3)_4,5H_2O + 2[Ba(NH_4)N(SO_3)_2,1\frac{1}{2}H_2O]$ could not possibly be admitted as in accordance with the microscopic appearance of the preparation.

Jacquelain, by adding diammonium imidosulphonate to a slight excess of baryta water, obtained a precipitate which he very fully analysed, and found to have the empirical formula

$$(NH_3)_2(BaO)_2(SO_3)_3.$$

Instead of this impossible formula, we venture to write

$$Ba_4(NH_4)N_3(SO_3)_6,3H_2O,$$

the formula of an eight-ninths barium ammonium imidosulphonate, since the calculated numbers agree still better with his analysis than those for his formula.

	Calculated.	Found. (Jacquelain).
Barium	47·99	48·26
Sulphur............	16·81	16·81
Nitrogen...........	4·90	4·97
Hydrogen	0·88	0·88

Using an ammoniacal solution of barium chloride instead of baryta water, he got nearly the same results.

Barium Potassium Imidosulphonate.—This is a nearly insoluble crystalline salt, preparable by heating dipotassium hydrogen imidosulphonate with baryta water. It has been described by Berglund, and was known to Fremy. We have not analysed it, and believe it has not been analysed by others.

Barium Sodium Imidosulphonate.—When barium chloride in dilute solution is very slowly added, with constant stirring, to an excess of trisodium imidosulphonate, a crystalline precipitate is formed which under the microscope is seen to be free from any admixture of tribarium imidosulphonate. It is alkaline to litmus, very sparingly soluble in water, readily in nitric or hydrochloric acid, and decomposed by ammonium carbonate to a large extent, but never completely. It contains water, but does not noticeably lose weight even at 120°. Heated quickly to a higher temperature, it is dissipated in a cloud of barium sulphate. Five preparations made at different times show close agreement in composition, with the exception of that first prepared (which is entered in our note book as not pure). The numbers agree with those calculated for $Ba_{11}Na_3N_{10}(SO_3)_{20},13H_2O$, which may be written as $8BaNaN(SO_3)_2,H_2O + Ba_3N_2(SO_3)_4,5H_2O.$

	Calculated.	a.	b.	c.	d.	e.
Barium ..	41·12	42·35	40·05	41·17	40·45—41·07	40·85—40·91.
Sodium ..	5·02	5·08	5·26	4·93	—	5·25
Sulphur ..	17·46	18·80	—	—	17·54	17·56

The barium and sodium were determined by cautious ignition of the salt alone, then with sulphuric acid, and boiling out with water. The residue was weighed as barium sulphate, and the soluble matter, after re-ignition, weighed as sodium sulphate. The sodium of d was lost. The sulphur was estimated by hydrolysis, followed by precipitation with barium chloride, but the barium sulphate was here weighed in two quantities, that formed by hydrolysis and that by the barium chloride.

Calcium Imidosulphonates, Simple and Double.

Normal calcium imidosulphonate, $Ca_3N_2(SO_3)_4$, is not formed by the action of calcium chloride on sodium or ammonium imidosulphonate. When a solution of diammonium imidosulphonate is treated with pure, soft calcium hydroxide in the calculated quantity, ammonia is at once liberated and is all expelled by two or three evaporations of the solution to dryness. The salt left dissolves, and forms concentrated solutions crystallising in transparent prisms. But although the salt dissolves at first freely, the last portions are more difficult to bring into solution, and it may be that water partly decomposes the salt into the calcium hydrogen salt and calcium hydroxide. The salt was not analysed, except that a calcium determination was made, from which it appeared that the crystals have 10 mols. H_2O to 2 atoms of nitrogen in the salt.

Calcium hydrogen imidosulphonate is obtained in radiating groups of fine needles when diammonium imidosulphonate and the calculated quantity of calcium hydroxide are mixed, and the solution repeatedly evaporated to expel all ammonia. The calcium hydroxide dissolves quickly after it is added. The salt is soluble, and has not been analysed.

Calcium ammonium imidosulphonate is a sparingly soluble salt, obtained when the calculated quantity of calcium hydroxide is dissolved in diammonium imidosulphonate solution, this quantity being in the proportion $Ca(OH)_2 : (NH_4)_2HN(SO_3)_2$. The salt rapidly crystallises after the dissolution of the lime. It has not been analysed.

Calcium Sodium Imidosulphonate.—To a hot concentrated solution of trisodium imidosulphonate a solution of calcium chloride is added, containing about the requisite quantity to form the tricalcium salt, and the mixture left to cool. It is not the tricalcium salt, however, but the calcium sodium salt, which crystallises out in groups of hard, brilliant prisms ; it can be recrystallised, and thus purified if necessary. It is sparingly soluble in cold water, and has an alkaline reaction. It only very slowly takes up carbonic acid from the atmosphere. Analysis corresponds to the composition $CaNaN(SO_3)_2,3H_2O$.

	Calculated.	Found.		
		I.	II.	III.
Calcium....	13·75	13·95	14·07	—
Sodium....	7·90	7·72	—	—
Sulphur....	21·99	—	22·21	—
Nitrogen...	4·81	—	—	4·88

The relative positions of the calcium and sodium are not very certain. For sake of symmetry, the sodium might be put in the imide relation, but such a procedure has nothing to support it. Taking the sodium to act as the more basylous element, the formula becomes

$$Ca \diagdown N \diagup \begin{matrix} SO_3Na \\ SO_3 \\ SO_3 \\ SO_3Na \end{matrix} \diagdown Ca.$$
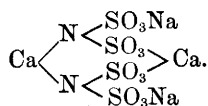
Lead Imidosulphonates.

A lead imidosulphonate was used by Jacquelain, and again by Berglund, to prepare imidosulphonic acid; but we know of no publication of particulars concerning the salt employed.

Disodium or other bibasic imidosulphonate does not yield a precipitate with lead nitrate, and only a very slight one with normal lead acetate. It is therefore necessary to take either the trisodium imidosulphonate, or to employ a basic lead acetate, in order to get an insoluble lead salt in sufficient quantity. This salt is always a basic or hydroxy-salt; so that its separation renders the mother liquor much less basic than the mixed solutions employed. Hence the retention of lead salt and imidosulphonate together in the mother liquors, and also the fact that either one or the other must be present in them. In fact, it is only by using a basic lead acetate that it is possible to throw all the imidosulphonate out of solution, whilst to precipitate all the lead, it is necessary to use the trisodium salt. Hydroxy-lead acetate, and lead nitrate or normal acetate yield precipitates of different salts with trisodium imidosulphonate, but the metal in the salt precipitated consists entirely of lead. One other point to be here noticed, as affecting precipitation, is the solubility in solution of normal lead acetate of the lead imidosulphonates insoluble in water. The solution is alkaline, and freely precipitable by carbonic acid, and may be regarded as containing basic lead acetate and the soluble lead hydrogen imidosulphate. Although a superficial examination of the reactions of imidosulphonates with lead salts may suggest the view of their being ill-defined, fuller investigation proves them to be quite definite.

The *normal salt*, $Pb_3N_2(SO_3)_4$, appears not to exist. The first addition of lead acetate or nitrate gives a precipitate of a basic salt with trisodium imidosulphonate ; and basic lead imidosulphonate, treated with small quantities of nitric acid, dissolves, as a whole, to yield a neutral or slightly acid solution, the undissolved part remaining unchanged (p. 971).

The *lead hydrogen salt*, $HN(SO_3)_2Pb$, appears to exist in solution, but the attempt to separate it leads to decomposition. Its solution can be prepared by treating either basic salt with somewhat less than enough dilute sulphuric acid, and decanting the clear solution from the sulphate and undecomposed basic salt. The solution can be preserved unchanged, in absence of acetates, for a very short time only. It is slightly acid to litmus. Left in a desiccator, it suffers decomposition into amidosulphonic acid and lead sulphate, slowly at first, but more rapidly as the solution grows concentrated. Heating the solution effects the same change. Alcohol produces a voluminous precipitate, gradually giving place to a crystalline deposit which partly adheres to the sides of the vessel, is nearly insoluble in water, and appears to be sulphate.

Hemihydroxy-lead Imidosulphonate, $HOPbN(SO_3PbOH)_2$.—When lead nitrate and trisodium imidosulphonate in solution are brought together in widely varying proportions, this salt is precipitated, voluminous at first, but soon becoming dense and granular. Disodium imidosulphonate and sodium nitrate are the other products of the reaction

$$3Pb(NO_3)_2 + 3H_2O + 4Na_3N(SO_3)_2 = (HOPb)_3N(SO_3)_2$$
$$+ 3HNa_2N(SO_3)_2 + 6NaNO_3.$$
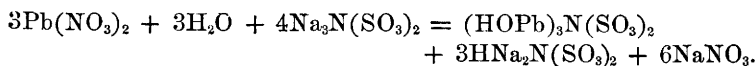
The precipitation is very nearly quantitative. If the trisodium salt is not used in excess, the mother liquors are neutral to methyl-orange.

Normal lead acetate may be used in place of the nitrate, but the results are not so satisfactory. The best way to proceed is to mix the solutions rapidly together in something approaching the right proportions; or the two salts may be rubbed together in the solid state and then treated with water. By either of these methods, if the proportion of either salt is not very many times greater than it should be, a product of constant composition is obtained, which differs, however, from the pure lead salt in having about $\frac{1}{73}$rd of the lead replaced by hydrogen. The weight of the precipitate obtained from a given quantity of trisodium salt is greater with lead acetate than with the nitrate, and greater as the excess of acetate used is greater. The acetate mother liquor, though alkaline to methyl-orange, is acid to phenolphthaleïn, and, after the lead in it is replaced by sodium, by precipitation with normal sodium oxalate,

can be titrated by sodium hydroxide, using phenolphthaleïn as indicator. Thus tested, these liquors proved to contain free acetic acid; the quantity increasing with that of the acetate used, and, therefore, with the precipitate produced. In these experiments, particularly good *normal* lead acetate was used. It appeared from the experiments made that about one-eighth of the excess of lead acetate used must react with disodium imidosulphonate, a product of the main reaction as already pointed out, the change being as follows:—

$$3Pb(OAc)_2 + 3H_2O + HNa_2N(SO_3)_2 = (HOPb)_3N(SO_3)_2 + 2NaOAc + 4HOAc.$$
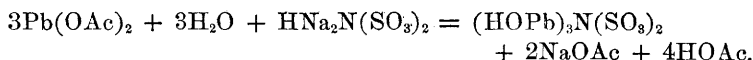
The acetic acid thus generated acting so as to reverse the reaction, is probably the cause of the very slight replacement of lead by hydrogen in the salt precipitated by acetate.

When the trisodium imidosulphonate solution is added by degrees to the lead acetate, a gelatinous precipitate, like lead hydroxide, forms and then redissolves in the lead acetate. When enough of the sodium salt has been added to cause a permanent precipitate, this is somewhat slimy, and only slowly becomes pulverulent, whilst the walls of the vessel get coated with a crystalline precipitate. The mixed product is unfit for analysis. When the lead acetate is added gradually to the sodium imidosulphonate, the precipitate also remains voluminous and somewhat gelatinous, 'and is probably not a pure product. If too much of the sodium salt has not been added, and the solution is quickly filtered, it slowly yields a few brilliant crystals of what is evidently, both from its appearance and the results afforded by an imperfect analysis, the hydroxy-lead salt.

The hydroxy-lead salt, in perfect, brilliant, microscopic prisms, can be obtained very pure by treating the more basic lead salt, next described, with but little more nitric acid than is required to remove the excess of lead. The nitric acid can be clearly seen to dissolve a portion of the more basic salt, and almost at once to deposit a crystalline precipitate and incrustation of the hemibasic salt. If, instead of stopping the addition of nitric acid when enough has been used, more is added, the crystalline salt proportionately dissolves without reprecipitating. The nitric solution is neutral to methyl-orange, so that, in the dissolution of the more basic salt, the reaction is

$$(HOPb)_3N(SO_3)_2,Pb(OH)_2 + 6HNO_3 = HPbN(SO_3)_2 + 5H_2O + 3Pb(NO_3)_2,$$
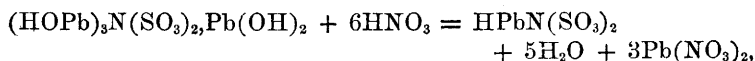
and then, this solution reacting with a further quantity of the more basic salt, gives

$$2(HOPb)_3N(SO_3)_2,Pb(OH)_2 + HPbN(SO)_2 = 3(HOPb)_3N(SO_3)_2 + H_2O.$$

3 Y 2
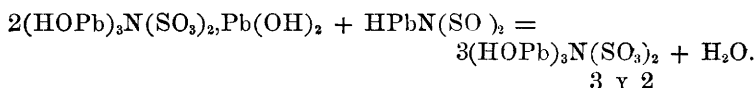
This, in a manner, can be shown by pouring the nitric solution into a large excess of hydroxy-lead acetate solution, when the hemi-hydroxy-lead imidosulphonate also precipitates in the pure state. There is also the fact observed that the nitric solution when soon poured off from the undissolved basic salt, contains much lead, whereas if it is left over the undissolved basic salt it goes on depositing a crystalline precipitate of the hemi-basic salt.

The modification of this process, expressed by the equation

$$3(HOPb)_3N(SO_3)_2,Pb(OH)_2 + HN(SO_3Na)_2 + 2HNO_3 = 4(HOPb)_3N(SO_3)_2 + 2NaNO_3,$$
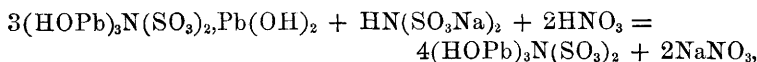
has also been successfully carried out by adding the nitric acid very slowly and shaking well.

The hemi-hydroxy-lead imidosulphonate is an anhydrous salt, not counting its hydroxyl, very permanent, losing nothing at 100°, insoluble in water, and scarcely, if at all, alkaline in reaction when in contact with wet litmus paper.

A number of preparations by different methods have been analysed with closely concordant results:

	Calculated.	Found.
Lead..........	73·40	73·21—73·35
Sulphur	7·56	7·50

The lead acetate precipitates gave from 72·31 to 72·78 per cent. lead, and from 7·52 to 7·65 per cent. sulphur. The sodium was determined in some of these preparations, and was found to be no more than 0·075 per cent.

The pure salt was also titrated with a standard nitric acid, and its basicity found to agree with that calculated. In order to just dissolve 1 gram of the salt leaving the solution neutral to methyl-orange, 48·71 c.c. of the acid was required, the calculated being 47·28 c.c.

Five-eighths Oxy-lead Imidosulphonate, $(HOPb)_3N(SO_3)_2,PbO$ or $Pb(OH)_2$.—This salt is precipitated on adding trisodium imidosulphonate to excess of basic lead acetate, the quantity of basic lead acetate needed being very large; it is advantageous to use not less than 6 mols. of hemi-hydroxy-lead acetate to 1 mol. of trisodium imidosulphonate. The calculated quantity is 5 mols., but an excess helps to keep sodium out of the salt. The reaction is as follows:—

$$Na_3N(SO_3)_2 + 5HO\cdot Pb\cdot OAc = (HOPb)_3N(SO_3)_2,Pb(OH)_2 + 3NaOAc + Pb(OAc)_2,$$
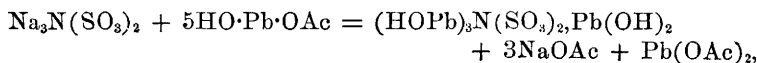
and, therefore, it would be better probably to employ a more basic lead acetate. Using, as we did, about 6 mols. of hemi-hydroxy-lead

acetate, the mother liquor, after precipitation, was still markedly basic. Both precipitate and mother liquor were quite free from sulphate; a very little sodium was found in the precipitate after it had been well washed, but no acetic acid. It is insoluble in water, but readily soluble in dilute nitric acid. Its partial dissolution in nitric acid leads to the formation of the hemi-hydroxy-lead imidosulphonate. It has scarcely any action on moist, red litmus, when left in contact with it. It is insoluble in solutions of the parent salts, and is not altered by them.

It does not lose water even when heated to 130°, but, at a higher temperature, it gives off, first water, then ammonia, then water again, then it blackens through formation of sulphide, and finally it evolves sulphur dioxide. The loss of water and ammonia is explained by the equation

$$3(HO)_5Pb_4N(SO_3)_2 = 6PbO + 3PbSO_3 + 3PbSO_4 + NH_3 + N_2 + 6OH_2.$$
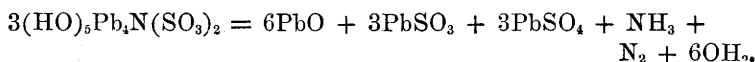
Then the lead sulphite becomes, as usual by the rising temperature, partly lead sulphide and sulphate, partly lead oxide, and sulphur dioxide. At the temperature of fusion, the sulphide and oxide would, of course, react.

Two preparations were analysed, a and b:

	Calculated for $(HOPb)_3N(SO_3)_2,PbO,\frac{1}{2}H_2O.$	Found.		
		$a.$	$b.$	$c.$
Lead............	76·81	76·79	76·05	76·82
Sulphur.........	5·94	5·82	6·00	—
Sodium	—	0·15	0·15	—

Behaviour of Imidosulphonates as Compound Amines towards other Bodies.

We have here collected some facts, already recorded in the paper, which appear to show that imidosulphonates form compounds in which the nitrogen becomes quinquevalent as in ammonium salts.

First, in order of observation, there is the retention of 1 mol. of water at 110° by the trisodium salt. The potassium salt, which crystallises with 1 mol. H_2O (Raschig), has not been examined in this respect. Next, there is the union of the diammonium salt with sodium nitrate to form a well-crystallised compound, which may be formulated as $\frac{H}{NO_3}{>}N{<}\frac{(SO_3Am)_2}{Na}$, and the similar compound of dipotassium imidosulphonate. Lastly, there is the more basic lead salt described in the last part of the previous section of this paper.

This may be written $\underset{O}{\overset{Pb}{|}} > N \ll \overset{(SO_3PbOH)_2}{PbOH}$ or $HO \cdot N \ll \overset{(SO_3PbOH)_2}{(PbOH)_2}$

according as we reject or admit the presence of 1 mol. of water, as shown by analysis.

Silver Imidosulphonates.

Silver nitrate and trisodium imidosulphonate yield three different compounds, in which 1, 2, and 3 atoms of sodium are replaced by silver.   Such an unusual behaviour in the salt of a polybasic acid gives to imidosulphonic acid a special interest.

The addition of silver nitrate in limited quantity causes a white precipitate which redissolves to be rapidly followed, unless the solutions are very dilute, by the separation of another compound.   This consists of interlacing, fibrous crystals, filling the liquid as a felted mass, even when the quantity present is small.
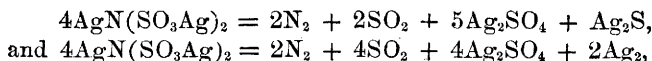
The addition of more silver nitrate to the liquid and crystals, generally causes more of the first white precipitate to be formed, and subsequently, if sufficient of it is added, the disappearance of both the precipitates together.   The new solution becomes almost immediately full of a third precipitate, this time of very dense, hard, minute, separate crystals, which rapidly subside as a deposit, in appearance closely resembling silver sand.   A salt of the same composition as this often occurs as a hard, crystalline incrustation on the sides and bottom of the beaker when a little silver nitrate is added to the mother liquor from the felted crystals.

Some experiments with tripotassium imidosulphonate have given us salts apparently analogous to those got from the sodium salt, but we have not further examined them.

Triargentic Imidosulphonate.*—By adding the sodium salt in limited quantity to silver nitrate, the white precipitate is also formed, and is now permanent in contact with the mother liquor.   This precipitate, which is triargentic imidosulphonate, is but very slightly soluble in water, and, after long washing on the filter, yields a milky filtrate. It is a relatively voluminous precipitate, forming chalk-like masses when dry.   It is without water of crystallisation, as was to be anticipated, but even when heated for a long time at 110° retains 0·55 per cent. of water (possibly fixed by hydrolysis from the atmosphere), as determined by combustion with copper oxide.   It bears heat well, but at a comparatively high temperature it rapidly decomposes with or without fusion, giving in the open tube first a very little ammonia and a slight sublimate, then sulphur dioxide,

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* May possibly have been already described by Berglund in the *Lunds univ. Arsk.*, **12**.

nitrogen, silver, silver sulphide, and silver sulphate. When heated in a vacuum, scarcely any sublimate is formed, and no change takes place till the temperature reaches 440°, when gas comes off, and blackening without fusion occurs; the residue consists of silver sulphate, silver sulphide, and silver, and the gas of nitrogen and sulphur dioxide. The proportions of these products vary a little, a higher temperature apparently giving more silver and sulphur dioxide. The first moiety of gas was thus found to consist of 4 vols. of nitrogen to 5 vols. of sulphur dioxide, and the second moiety of 2 vols. of nitrogen to 3 vols. of sulphur dioxide, so that the decomposition lies between those expressed by the equations

$$4AgN(SO_3Ag)_2 = 2N_2 + 2SO_2 + 5Ag_2SO_4 + Ag_2S,$$
$$\text{and } 4AgN(SO_3Ag)_2 = 2N_2 + 4SO_2 + 4Ag_2SO_4 + 2Ag_2,$$

but nearer the first one.

The salt was prepared for analysis by adding the sodium salt gradually, with stirring, to excess of silver nitrate. In spite of the strongly alkaline reaction of the former, the mother liquor of the precipitate proved to be neutral, as it should be; the precipitate was brilliantly white, without the slightest brown tinge. As it is not decomposed by water, it was well washed. Its analysis gave, besides the 0·55 per cent. water mentioned above, the following results:—

	$AgN(SO_3Ag)_2$.	I.	II.	III.
Silver..........	65·06	64·92	64·53	64·58
Sulphur........	12·85	—	—	12·94
Nitrogen.......	2·81	—	—	3·16

Found.

Diargentic Sodium Imidosulphonate.—The sandy precipitate, described above, is a salt with 2 atoms of silver to 1 atom of sodium. It is sparingly soluble in water, and very slightly decomposed by it, silver hydroxide being one of the products. It is of a faint buff colour. Under the microscope its crystals are seen to be hexagonal plates, always single; they act on polarised light. This salt, though otherwise anhydrous, retains a little water with the same firmness as is shown by the other silver salt; its behaviour when heated also closely resembles that of the latter, except that, naturally, sodium sulphate forms part of the residue as well as silver sulphate.

To prepare the salt for analysis, the sodium salt was added gradually to a little less than two-thirds of its equivalent of silver nitrate. The sandy precipitate obtained was only slightly washed, and then drained and dried on a tile. An incrustation (washed *in situ*) was also analysed. The results were:—

	$Ag_2NaN(SO_3)_2$.	Incrust.	Precip.
Sodium..........	5·57	5·61	5·67
Silver	52·30	52·02	51·87
Sulphur..........	15·50	—	15·60
Nitrogen	3·39	—	3·45

Argentic Disodium Imidosulphonate.—This salt, which forms crystalline fibres, is the most soluble of the three salts, but is still only sparingly so.   It is gradually and visibly decomposed by water, the change consisting, apparently, partly in the formation of silver hydroxide and hydrogen disodium imidosulphonate, partly in resolution into trisodium salt and the diargentic sodium salt.   On this account, although readily produced, it is difficult to get pure.   It retains a very little water, as usual, and behaves when heated almost like the preceding salt.   For analysis, it was freed from mother liquor by pressure in a calico filter, and then between porous tiles.   In preparing it, the sodium salt was added to a little less than one-third of its equivalent of silver nitrate, and the mixture agitated at once in order to redissolve the white precipitate of silver salt first thrown down, and before the fibrous crystals begin to form.   Analysis gave:—

	$AgNa_2N(SO_3)_2$.	*a.*	*b.*	*c.*	
Sodium	14·02	14·75	—	—	13·81
Silver	32·93	33·07	33·49	33·50	33·49
Sulphur	19·51	—	19·18	19·52	—
Nitrogen......	4·27	—	—	4·29	—

Double Mercury Imidosulphonates.

Single mercury imidosulphonates seem to be incapable of existence.

Mercury Potassium Imidosulphonates.—Berglund prepared mercury dipotassium imidosulphonate, $HgN_2(SO_3K)_4$, from tripotassium imidosulphonate.   We have prepared it from dipotassium imidosulphonate by adding mercuric oxide to it, heating the mixture with water, filtering hot if necessary, and leaving the solution to cool.   The salt, which is nearly insoluble in cold water, separates out in very minute needles, sometimes arranged loosely, sometimes in spherical tufts, and is, when dry, of silvery lustre.

An *oxymercuric potassium salt*, analogous to the sodium salt (p. 983), seems to be among the products of the reaction between mercuric nitrate and potassium imidosulphonates, but we have not made any study of it.

The behaviour of mercury dipotassium imidosulphonate with acids,

as observed by us, is of interest in connection with the theory of the constitution of these salts, and we shall refer to it later on when discussing that point (p. 986). When the salt, in the form of paste with water, is treated with nitric acid, it is converted into the very slightly soluble dipotassium imidosulphonate, all its mercury dissolving as mercuric nitrate. When washed and drained on a tile, the salt left undissolved was found to be free from mercury and from sulphate. The same experiment can be carried out by the use of dilute sulphuric acid, but less satisfactorily. The nitric acid used may be strong and in excess, but the sulphuric acid must be dilute and not in excess, and is apt to give a small precipitate of mercuric salt. Hydrochloric acid removes both metals, and causes extremely rapid hydrolysis.

Mercury Barium, $HgN_2(SO_3)_4Ba_2$, *and other Double Mercury Imidosulphonates.*—According to Berglund, mercury dipotassium imidosulphonate gives a series of double salts in which the potassium is replaced by another metal. It follows that these salts can also be prepared from the mercury sodium salts, but we have only made ourselves familiar with the mercury barium salt, particularly noticed by Berglund. It is a lustrous, crystalline, dense salt, almost insoluble in cold water.
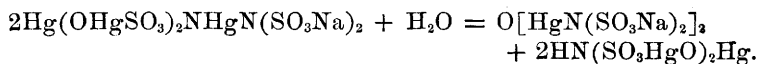
Mercury Dihydrogen Imidosulphonates.—When mercury barium imidosulphonate is treated with dilute sulphuric acid, not more than sufficient to remove the barium, it appears to be sharply converted into barium sulphate and mercury hydrogen imidosulphonate. This observation of Berglund's we have confirmed and extended. We worked quantitatively, and were careful to use the sulphuric acid in slight deficit, and to filter quickly. But, on testing the filtrate, we found the hydrolysis of the imidosulphonate into sulphate and amidosulphonic acid had already begun. It progressed steadily, and in 10 minutes a good deal of sulphuric acid had been formed, showing that mercury hydrogen imidosulphonate is even less stable than hydrogen imidosulphonate itself. In about 10 minutes also, the solution began to grow turbid, from separation of an oxymercuric salt, probably amidosulphonate. The fresh solution, when almost neutralised with potassium hydroxide, gave a slight, white turbidity, doubtless of oxymercuric potassium imidosulphonate; this dissolved when a little more alkali was added. The slightly alkaline solution, thus prepared, soon began to deposit minute crystals, which we identified as mercury dipotassium imidosulphonate. Thus, we had proved, so far as might be done, that the fresh filtrate from the barium sulphate is really a solution of mercury hydrogen imidosulphonate.

Oxymercuric Hydrogen Imidosulphonate.—A second salt of mercury

and hydrogen can be readily obtained which is at once both basic and acid, as its name indicates. Highly concentrated mercuric nitrate solutions, even when as free as possible from nitric acid, dissolve solid potassium or sodium imidosulphonates, yielding clear and comparatively stable solutions. When these solutions are heated, the imidosulphonate hydrolyses into amidosulphonate, but if diluted without heating they deposit oxymercuric hydrogen imidosulphonate. The same salt is almost immediately precipitated when trisodium imidosulphonate in solution is added to mercuric nitrate.

To prepare this salt, about 5 parts by weight of an undiluted mercuric nitrate solution are taken, equal to about half its weight of mercuric oxide, and into it, with stirring, is poured a cold solution (necessarily dilute) of 1 part of trisodium imidosulphonate; precipitation of the salt begins almost at once, and is finished in a few minutes. The mother liquor still contains much mercuric nitrate and some imidosulphonate, besides sodium nitrate and much nitric acid. The addition of a little more trisodium salt causes scarcely any further precipitation, but a larger quantity throws down the oxymercuric sodium salt. The brilliant white and voluminous oxymercuric hydrogen salt hydrolyses only very slowly in its acid mother liquor, on account of the protective action of the mercuric nitrate. It should be repeatedly washed by subsidence and decantation with abundance of cold water, and drained till dry on a tile or filter. If less mercuric nitrate has been used, and the precipitate contains sodium (as oxymercuric sodium salt), this may be converted into the pure oxymercuric hydrogen salt either by digestion for a day with concentrated mercuric nitrate solution and washing, or simply by continued and thorough washing with water. If digestion with mercury nitrate solution is adopted, the water used for the first washing must contain a little nitric acid to guard against the formation of any oxynitrate.

Oxymercuric sodium imidosulphonate, when washed with much water for a long time, leaves a far smaller weight of oxymercuric hydrogen salt, and imparts continuously to the wash-waters small quantities of a mercury sodium imidosulphonate, apparently the same as that got by digesting mercuric oxide in a solution of mercuric disodium imidosulphonate, perhaps $O[HgN(SO_3Na)_2]_2$. These washings are neutral or faintly alkaline, and when evaporated a little on the water-bath, yield small quantities of micaceous crystals. This reaction appears to be expressed by the equation—

$$2Hg(OHgSO_3)_2NHgN(SO_3Na)_2 + H_2O = O[HgN(SO_3Na)_2]_2 + 2HN(SO_3HgO)_2Hg.$$

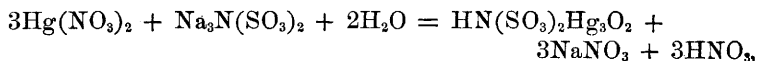Oxymercuric hydrogen imidosulphonate is an anhydrous salt.

After drying in a desiccator, it loses 0·7 to 0·8 per cent. of water when heated at 100° or above. It may be heated in dried air to 180° or higher without changing; but at a little below a dull red heat it decomposes, and then slowly gives off water, nitrogen, and sulphur dioxide; at this temperature it is yellow, but when cooled it again becomes white. At the softening point of hard glass, it melts to a dark red liquid, and effervesces, yielding sublimates of metallic mercury, mercurous and mercuric sulphates, and some other mercuric salt not sulphate and apparently nitrogenous. It seems impossible, even in a vacuum, to decompose it completely before the mercury sulphates themselves partly decompose. The gas first given off consists of nitrogen with half its volume or more of sulphur dioxide; subsequently it consists of nitrogen, sulphur dioxide, and oxygen. When rapidly raised to a red heat, the salt, at the moment of melting, effervesces and decomposes almost explosively.

Its reactions with sodium hydroxide and chloride, and with trisodium imidosulphonate are similar to those of the oxymercuric sodium salt (p. 984). Its basic or oxy-salt character is thus clearly demonstrated, independently of the evidence derived from analysis. The presence of hydrogen, other than that of hydration, is shown by first heating the salt for some hours at 180° in a current of dried air, and then to a much higher temperature, when water vapour, containing sulphuric acid, is given off. As the salt would yield only a little more than one-thousandth of its weight of hydrogen, and the isolation of the water would be difficult, hydrogen was not quantitatively estimated. The analytical results obtained were—

|	$HN(SO_3)_2Hg_3O_2$.	(a.)	(b.)
Mercury	74·35	74·03	74 09
Sulphur	7·93	8·06	8·(0
Nitrogen	1·73	1·76	1·65
Hydrogen........	0·12	—	—
(Sodium)	—	0·06	0·06
(Moisture)	—	0·20	0·13

The preparation a was made by the direct method; the other, b, was digested with mercuric nitrate to remove the sodium which it contained, and then washed with water slightly acidified with nitric acid.

On writing down the reaction by which this salt is formed from mercuric nitrate and trisodium imidosulphonate—

$$3Hg(NO_3)_2 + Na_3N(SO_3)_2 + 2H_2O = HN(SO_3)_2Hg_3O_2 + 3NaNO_3 + 3HNO_3,$$

and comparing it with the equation where oxymercuric sodium imido-

sulphonate is the product, it will be seen that in both cases the nitrate comes out half as sodium nitrate and half as nitric acid, and that the oxymercuric hydrogen salt may be represented as resulting from the reaction of the sodium salt with mercuric nitrate, thus :—

$$Hg(NO_3)_2 + NaN(SO_3)_2Hg_2O + H_2O = HN(SO_3)_2Hg_3O_2 + NaNO_3 + HNO_3.$$
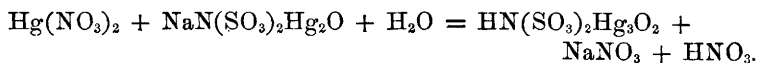
Now, this reaction can actually be realised, as already stated, but only with difficulty and in presence of great excess of mercuric nitrate solution, active probably by virtue of its free acid.   In the direct method of preparing the hydrogen salt, it is formed simultaneously with half as much again nitric acid as is produced when the sodium salt is formed.   From this it would appear that there is a point where, if the nitric acid is in sufficient quantity along with the mercuric nitrate, nitrogen takes or keeps hydrogen in place of mercury, and the second half of the sulphonic radicles, as well as the first, takes mercuric oxide in place of sodium, just as it does in other cases even in presence of free acid ; this, however, is difficult to determine by direct experiment with nitric acid, because of its liability to cause hydrolysis after a time, and of the uncertainty in knowing when the change sought for has occurred.

Mercury Sodium Imidosulphonates.—There are two mercury sodium imidosulphonates.   The monosodium salt is oxymercuric or basic, but the disodium salt is normal, and corresponds in composition with the potassium salt obtained by Berglund.

Unless gradually added to the solution of trisodium imidosulphonate, mercuric nitrate causes, almost immediately, a white, flocculent, crystalline precipitate, but this disappears on agitation so long as there is enough of the sodium salt remaining to keep the mixture alkaline or neutral ; when, however, this point is passed, the precipitate is permanent, and consists of *oxymercuric sodium salt*.   If the nitrate is added till neutrality is just reached, or nearly reached, the solution soon begins to deposit small, brilliant crystals, or does so after some evaporation. These are *normal mercuric disodium imidosulphonate*.   The addition of a solution of trisodium imidosulphonate to one of mercuric nitrate, free from any unnecessary excess of nitric acid, produces, as already stated, a white crystallo-flocculent precipitate which, if sufficient excess of nitrate remains, is the *oxymercuric hydrogen salt;* if there is too little nitrate, some oxymercuric sodium salt will be deposited as well.

Mercuric Disodium Imidosulphonate.—There is little to add concerning the preparation of this salt from the trisodium salt.   Here, as in other cases, it is better to have the mercuric nitrate solution highly concentrated, as then there need be but little excess of nitric acid.

To prepare this solution, moderately concentrated nitric acid is so far saturated with mercuric oxide that oxynitrate begins to form; it is then decanted from the excess of oxide and left to clarify by subsidence. If too much mercuric nitrate has been added to the sodium salt, the proportions can be successfully rectified by adding more sodium salt. The mercuric disodium salt can be purified, if necessary, by recrystallisation from hot water. Mercuric disodium imidosulphonate can also be readily prepared from disodium imidosulphonate and mercuric oxide. The two substances are triturated together in about the right proportions mixed with water, and warmed with it; the solution is then filtered, if necessary, and set aside to crystallise.

Mercuric disodium imidosulphonate crystallises in small, brilliant prisms always separate, quite permanent in the air, and sparingly soluble in cold water; the solution has a neutral reaction. The crystals contain 6 mols. H_2O, of which only four are lost in a vacuum at the ordinary temperature.

If heated at 100°, after exposure in a vacuum desiccator, it loses most of the remaining water, but not all, for then (and at higher temperatures, as 130°, more quickly), it increases slowly in weight by fixing atmospheric moisture, and becomes hydrolysed and strongly acid (see effects of heating dipotassium imidosulphonate, p. 954). If heated more strongly in an open tube, it yields a small sublimate of an ammonia-sulphite salt, mercurous sulphate, and mercury, sulphur dioxide and nitrogen being given off, and mercurous, mercuric, and sodium sulphates left as a residue.

When heated slowly in a Sprengel vacuum, it suffers change in a way that can be more closely studied. Even at 444°, no material alteration takes place, but just below a red heat it decomposes steadily, temporarily blackening through formation of mercuric sulphide, and giving besides much mercury as a sublimate, nitrogen and sulphur dioxide in the proportions of two volumes of the former to three of the latter, and a little very volatile white ammoniacal sublimate, together with a very little water, and another white sublimate volatilising again at 350—400°. The residue is sodium sulphate. That margin of the white sublimate which is more remote from the heat consists of mercurous sulphate, but the nature of the rest, which adheres firmly to the glass, is but imperfectly made out. It is a mercury compound scarcely affected by potassium hydroxide, boiling water, or dilute nitric acid, and seems to be a derivative of mercuric sulphate containing nitrogen.

The main changes by heat appear to be—

$$2HgN_2(SO_3Na)_4 = 4Na_2SO_4 + HgSO_4 + HgS + 2SO_2 + 2N_2,$$
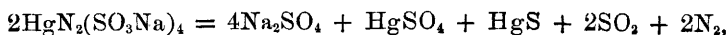
and then on further heating—

$$4Na_2SO_4 + 2Hg + 4SO_2 + 2N_2.$$
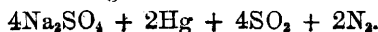
The ammoniacal sublimate and moisture are evidently due to water retained by the salt, probably through hydrolysis; whilst the mercurous sulphate is formed from mercury and mercuric sulphate.

With solutions of ordinary metallic salts, the mercuric disodium salt gives the various double mercury imidosulphonates noticed by Berglund. For example, with barium chloride it gives a precipitate of mercury barium imidosulphonate.

Sodium hydroxide precipitates mercuric oxide from the pure salt, but not in the presence of sodium imidosulphonate, and under any circumstances the precipitation of the mercury is far from complete. According to Raschig, Berglund found that mercuric dipotassium imidosulphonate gave no precipitate with potassium hydroxide, but in this respect we find that the potassium salt behaves like the sodium salt, except that the precipitate is perhaps smaller. Dilution lessens precipitation (see behaviour of mercuric oxide with trisodium imidosulphonate, p. 960). Ammonia gives a white precipitate; so also does ammonium chloride; in this case it is probably amidomercuric chloride. Mercuric oxide dissolves slightly in solution of the mercury sodium salt, rendering it alkaline. Both nitric acid and, still more so, hydrochloric acid dissolve the salt freely; apparently nitric acid does not immediately decompose it, but hydrochloric acid does completely. If the quantity of this acid is insufficient for the whole of the salt, its action is confined to its equivalent quantity, the rest of the salt being left undissolved, and no preferential replacement of the sodium or the mercury by hydrogen taking place. By extraction with ether, by evaporation, and by other tests, the change effected has been ascertained to be the formation of mercuric sodium chloride, sodium hydrogen sulphate, and amidosulphonic acid.

Analysis has given the following results:—

|	$HgN_2(SO_3Na)_4,6H_2O.$	Found.	
Mercury....	26·74	27·16	
Sodium	12·30	12·35	
Sulphur....	17·11	17·19	
Nitrogen ...	3·74	3·95	
Water	14·44	13·15	$\begin{cases} 8\cdot86 \text{ lost } in\ vac. \\ 4\cdot29 \quad ,, \text{ at } 100^\circ. \end{cases}$

The exposure in the vacuum was for 40—45 hours; the further loss at 100° was the greatest obtainable in undried air, longer heating being followed very slowly by increase of weight. As analysed, the salt shows nearly a tenth less than the water calculated. Efflorescence of the sample was not noticed, but may have occurred to a slight extent. The main cause of the deficiency is, without doubt, fixation

of some of the water of crystallisation or of atmospheric moisture by hydrolysis.

Oxymercuric Sodium Imidosulphonate.—In the preparation of this salt, the sodium imidosulphonate is taken in twice the molecular proportion to the mercuric nitrate; the result is satisfactory. The highly acid mother liquor retains much of the salt in solution, but it is thrown down if it is nearly neutralised with sodium hydroxide, and then contains scarcely any other mercuric or imidosulphonic salt. There is, however, no necessity to adhere closely to the calculated proportions, provided the sodium salt is neither in quantity great enough to redissolve the precipitate as mercuric disodium salt, nor so small as to leave the nitrate in great excess; it is, however, better to use too little than too much of the nitrate, especially if its solution contains any quantity of free acid.

Any precipitation of oxynitrate which water alone would cause in the solution of mercuric nitrate, is prevented by the presence of the sodium imidosulphonate, as this salt forms its basic mercury derivative by liberating half the nitric acid of the nitrate that it decomposes, and this acid is more than enough to keep any remaining nitrate from passing into oxynitrate; consequently, the washed precipitate is always free from nitrate. It may be washed sufficiently with water, which only very slightly acts on it, and may then be dried, either on paper or better on a tile.

On attempting to form a third and intermediate mercury sodium salt, which was to have the formula $O[HgN(SO_3Na)_2]_2$, analogous to the oxynitrate, $O(HgNO_3)_2$, we got, instead, only the two other salts, one in solution, the other as a precipitate. The oxymercuric sodium salt was thus obtained from a solution which, from first to last, was never acid, even the mother liquor being still faintly alkaline. The sulphonate and nitrate were used in the proportion

$$2NaN(SO_3Na)_2 : Hg(NO_3)_2;$$
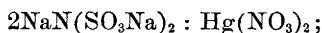
the nitrate was added gradually, with stirring, to the dilute solution of the sulphonate, and simultaneously a solution of sodium hydroxide was run in, in the proportion of nearly five-sixths of a molecular quantity. In this way much yellow mercuric oxide was formed, along with the white precipitate, but by prolonged stirring, the precipitate lost all tinge of yellow. The mother liquor now contained much disodium mercury imidosulphonate, and the precipitate, washed and drained on a tile, proved to be pure oxymercuric sodium imidosulphonate (analysis d). Allowing for sodium hydroxide used in neutralising the free nitric acid present in the mercury nitrate solution, the reaction appears to be that expressed by the equation

$$6NaN(SO_3Na)_2 + 6Hg(NO_3)_2 + 4NaOH = 2HgN_2(SO_3Na)_4$$
$$+ Hg(OHgSO_3)_2NHgN(SO_3Na)_2 + 12NaNO_3 + 2H_2O.$$
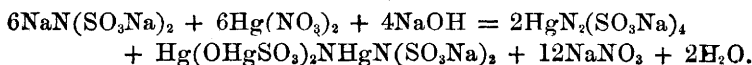
Oxymercuric sodium imidosulphonate contains water of crystallisation, and appears to be slightly efflorescent; otherwise, it is permanent for a long time, whether wet or dry, though ultimately it decomposes and becomes yellowish-brown. Protracted washing with water decomposes it, as does also digestion with concentrated mercuric nitrate solution, a residue of the hydrogen oxymercuric salt being left in both cases (p. 978). It is very stable if but moderately heated, losing nearly the whole of its water of crystallisation.

At about 135° it permanently changes colour slightly, and at a much higher temperature melts to a dark, red-brown liquid and effervesces, decomposing in a way essentially the same as that of the normal mercury sodium salt. Even very gradual heating in a current of dried air, at a temperature of 170°, fails to expel more than four-fifths of the water, in consequence, no doubt, of hydrolysis.

It is much more readily dissolved by hydrochloric acid than by nitric or sulphuric acid. From its hydrochloric acid solution it cannot be recovered by neutralisation, being almost instantly decomposed, like the normal mercuric sodium salt. It is converted by sodium hydroxide into insoluble mercuric oxide, and mercuric disodium imidosulphonate, which remains dissolved. Its basic composition is at once demonstrated by the action on it of sodium chloride, which leaves insoluble mercuric oxide, and dissolves the rest, probably, as the two salts, mercuric sodium imidosulphonate and mercuric sodium chloride. Trisodium imidosulphonate dissolves it, but not to a large extent. If the solution of this salt is concentrated, a little mercuric oxide may separate, but the addition of water causes this gradually to dissolve. When, however, the trisodium salt is added to the oxymercuric sodium salt, still in its mother liquor, free dissolution at once occurs; but without the mother liquor, the reaction is as above stated.

The composition of the salt may be expressed, as shown by the following analytical results, by the formula $OHg_2N(SO_3)_2Na,(OH_2)_2$, which has, however, to be doubled to represent its constitution. The water comes out low, partly because of loss by efflorescence, but mainly by getting fixed through hydrolysis.

	Calculated.	(a.)	(a.)	(b.)	(c.)	(d.)
Mercury	61·63	62·18	61·22	61·56	—	61·73
Sodium	3·54	3·87	4·14	3·97	3·57	3·56
Sulphur	9·86	10·23	10·06	10·03	—	9·79
Nitrogen........	2·16	—	2·27	2·24	—	—
Water	5·55	—	4·44	—	4·88	4·58

The preparation, a, was precipitated from 3 mols. of mercuric nitrate by 2 mols. of imidosulphonate, whilst b was got by adding
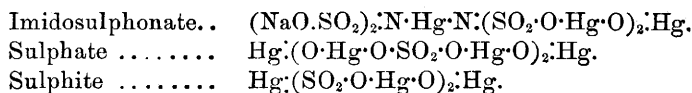
sodium hydroxide to the decanted mother liquor of a. The preparation, c, was precipitated from 2 mols. of nitrate by 1 mol. of imidosulphonate, and d was formed with a non-acid mother liquor. All preparations, as well as their mother liquors, were free from sulphate.

The formation of oxymercuric sodium imidosulphonate is expressed by the equation

$$4Hg(NO_3)_2 + 2NaN(SO_3Na)_2 + 2H_2O =$$
$$Hg(OHgSO_3)_2NHgN(SO_3Na)_2 + 4NaNO_3 + 4HNO_3.$$
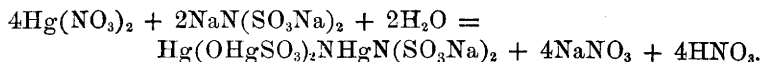
This reaction is noticeable for being one in which the sodium in the precipitate is not removed by the nitric acid ; but, if imidosulphonic acid be regarded as a weaker acid than nitric acid, the precipitation of potassium nitrate by tartaric acid or perchloric acid is quite as remarkable, whilst if, as is most probable, it is like sulphuric acid, then the retention of the sodium is only natural. It is hardly noticeable for the precipitation of a basic salt with production of nitric acid, since similar reactions are common with oxygenous mercuric salts.

In its constitution, as regards the oxylic mercury, oxymercuric sodium imidosulphonate resembles oxymercuric sulphate and oxymercuric sulphite, as represented in the following formulæ (Trans., 1886, **49**, 553) : —

Imidosulphonate..	$(NaO.SO_2)_2\dot{:}N\cdot Hg\cdot N\dot{:}(SO_2\cdot O\cdot Hg\cdot O)_2\dot{:}Hg.$
Sulphate	$Hg\dot{:}(O\cdot Hg\cdot O\cdot SO_2\cdot O\cdot Hg\cdot O)_2\dot{:}Hg.$
Sulphite	$Hg\dot{:}(SO_2\cdot O\cdot Hg\cdot O)_2\dot{:}Hg.$

Constitution of the Mercury Imidosulphonates.

From the widely established character of the relation between mercury and the nitrogen of ammonia and cyanogen, and from that of the mercury in its oxygenous salts, particularly those of sulphuryl, such as sulphites and sulphates, the relations of mercury in its imidosulphonates become of much interest, as likely to differ from those of other basylous elements.

Firstly, as to the mercury disodium and mercury dipotassium imidosulphonates, no hesitation will be felt in accepting for these salts—say that of sodium—the formula $HgN_2(SO_3Na)_4$ (Berglund). Yet this point is not so simple as it seems. Calcium forms the salt, $CaNaN(SO_3)_2$; silver forms the salt, $Ag_2NaN(SO_3)_2$; and mercury itself, the salts, $OHg_2NaN(SO_3)_2$ and $O_2Hg_3HN(SO_3)_2$. All these salts have only one-third of the bases either as sodium or hydrogen, and it will be well, therefore, to briefly review the reasons for writing $HgN_2(SO_3Na)_4$.

Disodium hydrogen imidosulphonate is a salt neutral, or only slightly acid to, litmus, although active as an acid, and, therefore, it cannot contain the group, SO_3H, since this always gives to its compounds acidity and a strong action on blue litmus. It must, therefore, be written $HN(SO_3Na)_2$. Mercury readily takes the place of the hydrogen of this salt, or of 1 atom of the sodium of the alkaline trisodium imidosulphonate, and the resulting mercury disodium salt is neutral in reaction. Transposition of the metals cannot be admitted to take place in its formation for two reasons. One is, that the alkaline reaction of the trisodium salt disappears when it becomes the mercury sodium salt, and there is no accounting for this if the mercury displaces the sulphonic sodium. The other reason is, that if the mercury takes the sulphonic relation in the salt, this salt would be an exception to the observation that all the oxylic mercuric salts capable of existing in presence of water are insoluble basic or oxysalts.

This theory of the constitution of the normal mercury double sulphonates accords with the interesting behaviour of these salts towards acids and alkalis. The latter only partially precipitate mercuric oxide from them, because the mercury is in immediate relation with (unoxidised) nitrogen. Nitric acid, which can replace the mercury by hydrogen, cannot do the same with the potassium or sodium, because this is in oxylic relation to sulphuryl, as it is in sulphates, and is, therefore, irremovable by this acid. Sulphuric acid also first replaces the mercury by hydrogen, when acting on the mercury potassium salt, although from the mercury barium salt it first takes the barium away.

Berglund would have chemists regard mercury imidosulphonates as salts of an independent acid, in which mercury is combined with special force. A fuller knowledge of the imidosulphonates does not tend to support this view. There are other series of double imidosulphonates besides that of mercury, apparently the only one observed by him: normal mercury hydrogen imidosulphonate has even less stability than imidosulphonic acid itself; oxymercuric hydrogen imidosulphonate is far more stable; dipotassium and disodium hydrogen imidosulphonates have equal or greater claims to be treated as particular acids; lastly, it is highly probable that, powerfully as mercury takes the place of hydrogen in ammonia itself, it will have little of that power when two-thirds of that hydrogen have already been replaced by sulphonic radicles.

The constitution of the salt in which two-thirds of the base of the trisodium salt are replaced by mercury next requires attention. It might be treated as having the single atom of sodium in the odd basylous position, that is, united to the nitrogen; but against this

four objections present themselves.   One is that it is highly improbable that the sodium should hold the imidic relation rather than the sulphonic.   A second is that it is quite as unlikely that a mercury atom should be united half to nitrogen and half to oxygen, whilst it is usual to find it thus united at once to oxygen and to an oxygenous radicle.   A third objection is, that whereas in other cases sulphuryl takes $1\frac{1}{2}$ atoms of mercuric oxide to saturate either of its valencies, it does not do so in this salt unless the sodium is given to one of the sulphuryls of the salt.   The fourth objection lies in the great improbability that sodium in the imidic relation would resist, as it here does, displacement by hydrogen on treating the salt with nitric acid.   Avoiding these four difficulties by placing one-fourth of the mercury with the nitrogen, there remains the usual $1\frac{1}{2}$ atoms to unite with half one of the sulphuryls.   The relations of the salt, and its constitution as here developed, require that its formula should be double that expressed in the lowest terms, in order to allow of the oxylic mercury being shown apart from the non-oxylic

$$Hg\ddot{.}(O\cdot Hg\cdot O\cdot SO_2)_2\ddot{.}N\cdot Hg\cdot N(SO_3Na)_2.$$
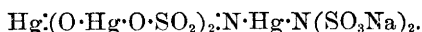
It now becomes clear that the sodium resists the action of nitric acid, because it is in oxylic relation to sulphuryl, as pointed out in discussing the constitution of the normal mercury disodium salt; that nitric acid removes a fourth of the mercury, replacing it by hydrogen, because this fourth part is in relation to the nitrogen; that nitric acid does not remove the rest of the mercury, because this exists as the oxymercuric group found in sulphate and sulphite, in oxylic relation to sulphuryl, also resisting the action of nitric acid; and, lastly, it becomes clear how it is that the oxymercuric hydrogen imodosulphonate has quite consistently a constitution different from that of the oxymercuric sodium salt, and how the one salt is formed from the other (compare Divers and Shimidzu, "On Mercury Sulphites," Trans., 1886, **49**, 574).

In fact, the constitution of the oxymercuric hydrogen imidosulphonate follows obviously from the production of the salt by (acid) mercury nitrate in excess.   From what we actually can observe in the case of the normal mercury dipotassium salt, we know that nitric acid of itself should act as represented by this equation :—

$$Hg(OHg\cdot O\cdot SO_2)_2NHgN(S_3ONa)_2 + 2HNO_3 =$$
$$Hg(OHg\cdot O\cdot SO_2)_2NH + HN(SO_3Na)_2 + Hg(NO_3)_2,$$
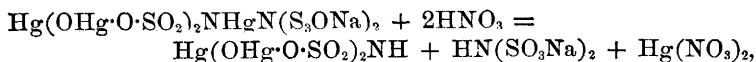
replacing the imidic mercury by hydrogen, but not touching the oxymercuric group in conformity with its inability in other cases (sulphites and sulphates) to do so when the group is joined to sulphuryl.   In the absence of mercuric nitrate, this reaction is

3 z 2

slowly followed by hydrolysis of the disodium hydrogen salt through the unadvoidable excess of nitric acid, but in presence of mercuric nitrate hydrolysis does not take place.   The mercuric nitrate finishes the formation, just formulated, of the oxymercuric hydrogen salt, in the way shown by the equation

$$HN(SO_3Na)_2 + 3Hg(NO_3)_2 + 2H_2O = HN(SO_2 \cdot O \cdot HgO)_2Hg$$
$$+ 2NaNO_3 + 4HNO_3,$$
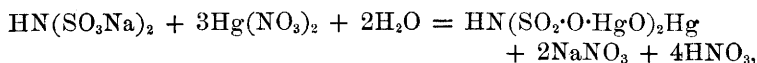
from which equation it will also be sufficiently clear how the whole change can be effected by mercuric nitrate without any addition of nitric acid.

From the constitution given to this salt, it is at once evident why it can be left for days in a nitric acid solution of mercuric nitrate without becoming hydrolysed ; for hydrolysis can only occur when some of the sulphonic group becomes acid, or SO_3H, and here the nitric acid, especially in presence of much mercuric nitrate, is powerless to displace the oxymercuric group by hydrogen.

There remains now only to tabulate the three mercuric salts, the constitution of which has been discussed, in order to bring out their relations quite clearly, and particularly the intermediate relation of the oxymercuric sodium salt :—

Imidosulphonate.	Formula.
Mercuric disodium	$Hg{<}{N(SO_3Na)_2 \atop N(SO_3Na)_2}$.
Oxymercuric sodium....	$Hg{<}{N(SO_3Na)_2 \atop N(SO_3 \cdot Hg \cdot O)_2Hg}$.
Oxymercuric hydrogen..	$HN(SO_3 \cdot Hg \cdot O)_2Hg$.

ADDENDUM.

Oxyamidosulphonates.—In our last paper sent to the Society, which appeared in the Journal so far back as 1889, we had to call attention to the discrepancy between some of the results of the work on *sulphazotised salts* done by others and by ourselves.   We are glad to be able now to bring in support of the accuracy of certain of our own statements, the testimony of Dr. Raschig, who wrote, soon after the appearance of the paper on *oxyamidosulphonates,* to request us, when next publishing, to make known that he now entirely agrees with our account of the decomposition of oxyamidosulphonates by caustic alkali (Trans., 1889, **55**, 765), and withdraws his own statement concerning it, which was based upon qualitative reactions only.