CX.—*Amidosulphonic acid.*

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AMIDOSULPHONIC acid, erroneously supposed to be known nearly 40 years ago, was not actually discovered and prepared until 1876, by Berglund, and has only attracted the attention of chemists to any extent since 1887, when Raschig made known an easy way of preparing it by a new process.

The contents of this paper comprise a summary, not elsewhere found, of the work of others; new ways of forming the acid; a study of the interaction of oxyamidosulphonic acid and sodium amalgam, and of the same acid and sulphur dioxide; improvements in known methods of preparing amidosulphonic acid; a very productive and economical method of preparing it; some of its properties hitherto undescribed; some new salts of it; remarkable points in the behaviour of its silver and mercury salts; and an investigation of the decomposition of the acid by heat.

Our colleagues, Professors Sakurai, Loew, and Takahashi, have helped us in adding to what was known of the acid, the first-named by investigating its molecular conductivity, the other two its physiological action. Both these investigations have a special interest, and form the subjects of separate communications following this.

Name of the Acid.—Berglund accepted *sulphamic acid*, then in use, as an alternative name for the acid he had discovered, but employed that of *amidosulphonic acid.* This name, the use of which is now general, is analogically incorrect, and needs to be changed into either *aminesulphonic acid* or *amidosulphuric acid.* Similarly, imidosulphonic acid and nitrilosulphonic acid should be altered to amine-

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* This preparation was found to be damp when analysed.

† The numbers obtained for univalent and bivalent mercury in this case, namely, 51·98 and 21·48 per cent., are in accordance with the others, but as they were determined in the salt after it had been hydrolysed, they are not trustworthy, and therefore withheld from the table.

disulphonic and aminetrisulphonic acids, or to imidosulphuric and nitrilosulphuric acids. But it seems of little moment to make the change so long as ethylsulphonic acid remains in use in place of ethanesulphonic acid, and ethylsulphuric acid is misapplied to ethyl hydrogen sulphate. *Sulphamic acid* must remain in the background until such time as sulphimic acid becomes acceptable for imidosulphuric acid, and some analogous name has suggested itself as suitable for nitrilosulphuric acid.

Formation of the Acid.

1. Sulphur trioxide and ammonia, if the latter is kept in large excess, sometimes yield, according to Berglund, a very little ammonium amidosulphonate along with the imidosulphonate which is the chief product. He gives no details of his method of testing for it, and, before he states that he had occasionally found it in very small quantity, he guardedly says that probably it can be formed in this way. The difficulty presents itself that, even at 135°, ammonium amidosulphonate begins to change into imidosulphonate, whilst the temperature caused by the union of sulphur trioxide and ammonia is much higher than that, and Berglund mentions that he did nothing to keep down the temperature. But, although the amidosulphonate does begin to change at so low a temperature as 135°, a little of it can remain unchanged at temperatures not very far below 300°. So that, on the whole, when it is considered that it was Berglund who first recognised that the product of the interaction of sulphur trioxide and ammonia is not amidosulphonate but imidosulphonate, it seems wise to accept as well founded his assertion that occasionally amidosulphonate is also formed in very small quantity.

2. Ammonium imidosulphonate readily hydrolyses into the amidosulphonate (Berglund, 1876). The imidosulphonate is obtainable from chlorosulphonic acid, from pyrosulphuryl chloride, and from sulphuryl chloride (after the action of water), as well as from sulphur trioxide and ammonia.

3. Sulphamide, which is a product of the interaction of sulphuryl chloride and ammonia (Regnault, W. Traube), is decomposed by alkalis into amidosulphonate and ammonia (Traube, 1893).

4. By acting on acetonitrile with fuming sulphuric acid, a derivative of amidosulphonic acid, namely, acetyl acetamidinesulphonic acid, is obtained, and this hydrolyses, with extreme readiness, into diacetamide and amidosulphonic acid (Eitner, 1892).

In the above four cases, amidosulphonic acid comes out as a sulphuric derivative; in those which follow it comes from sulphur dioxide. In the first of them imidosulphonates appear again.

5. Nitrites, fully sulphonated by sulphur dioxide, become nitrilo-

sulphonates, which very easily hydrolyse into imidosulphonates, and these, again, can be hydrolysed into amidosulphonates (Berglund, 1876). The hydrolysis of potassium imidosulphonate was studied by Fremy and by Claus and Koch long before Berglund, but without amidosulphonic acid being discovered by them. Its production was overlooked, no doubt, through the great solubility of its potassium salt, and through its being liable to be destroyed by further hydrolysis.

6. Oxyamidosulphonic acid is produced by the hydrolysis of oximidosulphonic acid, which is formed by the sulphonation of a nitrite, and, by reducing this acid with sodium amalgam, sodium amidosulphonate is obtained (Berglund, 1876). Berglund's work was admittedly incomplete; he did not isolate the acid, and he did not state the conditions for success. Oxyamidosulphonic acid is not attacked by sodium amalgam, except in acid solution, and we have proved that it is then changed into amidosulphonic acid, having obtained crystals of the latter in this way. Zinc and sulphuric acid, or the Gladstone-Tribe copper-zinc couple, may also be used with perfect success for the reduction. Another, but indirect, way of effecting the conversion is given lower down (10).

7. Potassium nitrososulphate, which is prepared from potassium sulphite and nitric oxide, and is not a sulphonate, also yields amidosulphonic acid among the products formed when it is reduced by sodium amalgam (see p. 1615).

8. The simplest and most direct of all the processes for preparing amidosulphonic acid is the sulphonation of hydroxylamine, which may be effected by allowing sulphur dioxide to act long enough on a solution of one of its salts (Raschig, 1887).

9. Acetoxime also yields amidosulphonic acid, when treated with aqueous sulphur dioxide (M. Schmidt, 1891). Sodium metasulphite acts on the oxime to form a hydrolysable compound (v. Pechmann, 1887), dimethylmethyleneimidosulphonic acid (a monosulphonic, and, therefore, an amidosulphonic, not imidosulphonic, derivative), and this, on hydrolysis, yields acetone and amidosulphonic acid (Krafft, Bourgeois, and Dambmann, 1892).

10. The reduction of oxyamidosulphonic acid by sodium and by zinc has already been treated of (6), but this acid can also be converted by sulphur dioxide into imidosulphonic acid, from which amidosulphonic acid may be obtained by hydrolysis. That this would be the case was recognised by Raschig, but he did not attempt to effect the change. We find that when a solution of potassium oxyamidosulphonate mixed with a molecule of potassium hydrogen carbonate is submitted to the action of sulphur dioxide, as in sulphonating potassium nitrite, it is converted, apparently completely,

into the sparingly soluble, two-thirds normal potassium imidosulphonate. The conditions resemble those of the sulphonation of hydroxylamine, for the change is not immediate, but requires hours for completion at the common temperature, whilst at or near 0° it seems not to take place at all.

Methylic sulphate and ammonia do not form methylic amidosulphonate, as they were long supposed to do, but primary, secondary, and tertiary methylammonium sulphates and ammonium sulphate (Berglund, 1876). Ammonia acts, therefore, on an alkylic sulphate, as Berglund pointed out, in the same way as it does on an alkylic nitrate (Carey Lea, 1860). Although the nature of the interaction of ammonia and methylic sulphate was discovered and worked out in detail by Berglund, his name is not even mentioned in connection with the subject in chemical literature, as represented by Beilstein's *Handbuch* and Morley and Muir's *Dictionary*. The whole credit of the discovery is given to Claesson and Lundvall, and it is remarkable that, although these chemists dated their paper from Lund, in 1880, only four years after Berglund's memoir on amidosulphonic acid had appeared in that university town, they make no reference to it. In all points, so far as methylic sulphate and ammonia are concerned, Claesson and Lundvall had been anticipated by their countryman, except that they improved on Berglund's process of dissolving the alkylic salt in ether and passing gaseous ammonia into the solution, by first saturating the ether with ammonia and then adding the sulphate gradually, and, in this way, reduced to a minimum the production of the secondary and tertiary ammonium salts. The only chemists who worked on the action of ammonia on methylic sulphate before Berglund were Dumas and Peligot, in 1836, and they only observed that the two substances interact violently, when an aqueous solution of ammonia is added to the undiluted methylic sulphate, and, without giving quantitative analyses of the products, represented them to be methylic alcohol and methylic amidosulphonate ("sulphomethylane"). Strecker, in 1850, had, indeed, found that ethyl sulphate and ammonia combine, giving what he called *ammonium sulphethamate;* and it used, therefore, to be supposed that the action of ammonia on that sulphate was quite different from what it was on methylic sulphate. Strecker, however, did observe that his complex salt gave ethylamine when heated, although, from this weighty fact, he deduced nothing.

Preparation of the Acid.

Amidosulphonic acid may be advantageously prepared in two ways, one being based upon the sulphonation of hydroxylamine, and the other upon the hydrolysis of imidosulphonic acid. Although both hydroxylamine and imidosulphonic acid are obtainable in several ways, the best for both of them is the sulphonation of sodium nitrite, and hydrolysis of the suitable sulphonate. It is, therefore, from sodium nitrite that amidosulphonic acid will, on economical grounds, be prepared in either case. The production of the acid through imidosulphonic acid is much more profitable as regards time, labour, and yield, than its production through hydroxylamine; but at present it must be taken into consideration that hydroxylamine hydrochloride is at hand in most laboratories, and that if we take this as the starting point, it is easier to prepare the acid from it than to begin with sodium nitrite. This renders the hydroxylamine method the most convenient, pending the time when amidosulphonic acid itself becomes purchasable.

Preparation from Hydroxylamine Sulphate.—Raschig's account of this process, using the hydrochloride, is brief, and as follows. "Saturate an aqueous solution of hydroxylamine hydrochloride with sulphur dioxide, allow it to stand some time, and then evaporate until a pellicle of crystals forms. A large quantity of the acid crystallises out by cooling, and the mother liquor yields a little more, but mixed with ammonium sulphate." Krafft and Bourgeois (1892) used the solution of hydroxylamine hydrochloride very concentrated, saturated it with sulphur dioxide to begin with, and, for a day or two, supplied more as needed. In this way they got fully three-sevenths of the calculated quantity of the acid to crystallise out without any evapora-

Although sulphur dioxide takes some hours to complete its action on hydroxylamine, it acts rapidly at first, and occasions a sensible rise of temperature. Cold checks its action, and at 0° there appears to be none. Saturation of the hydroxylamine solution at this temperature with sulphur dioxide is sufficient, once for all, unless it is a very concentrated one, or is left exposed to the air. Some of the amidosulphonic acid becomes hydrolysed, if the solution is evaporated on the water bath, but there is no appreciable decomposition if it is evaporated in the cold.

Two points had to be investigated, the one being as to whether the acid of the hydroxylamine salt had any influence on the reaction, and the other whether hydroxylamine and sulphur dioxide suffer complete conversion into amidosulphonic acid, or yield other products, such as ammonium sulphate, nitrogen, or nitrous oxide. The outcome of these investigations was that the action of sulphur dioxide is quantitatively the same, whether the hydrochloride, the sulphate, or the base itself is used, and that, besides amidosulphonic acid, ammonium hydrogen sulphate is the only other direct product of the action. Very closely, about one-tenth of the hydroxylamine always becomes ammonia, the solution being cold (not much exceeding 25°), and of moderate concentration. When the solution, a day after preparing it, is distilled with potassium hydroxide, it gives a tenth of the nitrogen as ammonia, whether sulphate or hydrochloride has been used, or, whether or not, along with either of these salts, just enough sodium carbonate has been added to combine with its acid, leaving the hydroxylamine free, or whether more sodium carbonate has been added and converted into metasulphite. If, instead of at once distilling off the ammonia, the solution, deprived of its excess of sulphur dioxide, is heated for some hours at 150—160°, so as to hydrolyse all the amidosulphonic acid, and it is then distilled with potassium hydroxide, the ammonia obtained is closely equivalent to the hydroxylamine taken; no nitrogen, therefore, has been lost as gas. The stability of amidosulphonic acid is such that the decomposition of the acid is quite insignificant, and, therefore, that nearly all the ammonium hydrogen sulphate comes directly from hydroxylamine, sulphur dioxide, and water.

Although the action of sulphur dioxide on hydroxylamine is not affected by the acid present, there are several circumstances which make it advantageous to use the sulphate rather than the hydrochloride in preparing amidosulphonic acid. In the first place, the sulphate is easy to get in large crystals, which are practically non-deliquescent, and it is a much cheaper salt to prepare*; in the second place, sulphuric acid very greatly reduces the solubility of amidosulphonic acid in water, and hydrochloric acid hardly at all.

To prepare amidosulphonic acid from hydroxylamine sulphate, it is dissolved in four or five times its weight of water, the solution nearly saturated ice-cold with sulphur dioxide, and set aside at the ordinary temperature for a day in a flask closed not quite air-tight; the sulphur dioxide remaining is then expelled by a current of air, and the solution placed in a good desiccator, where the acid soon begins to crystallise out in thick plates. The crystals are well drained, and washed two or three times with a little ice-cold water. The yield should approach four-fifths of the weight of the hydroxylamine sulphate. As, however, amidosulphonic acid itself can be obtained from sodium nitrite more easily than hydroxylamine sulphate can, it will never be prepared from the latter on the large scale.

Preparation of Amidosulphonic acid from Sodium Nitrite through Imidosulphonic acid.—Briefly, this process consists in fully sulphonating sodium nitrite by means of sulphur dioxide and sodium carbonate, hydrolysing the nitrilosulphonate to acid sulphate and amidosulph-

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* See "Economical Preparation of Hydroxylamine Sulphate," p. 1665.

onic acid, neutralising with sodium carbonate, separating the sodium sulphate by crystallisation, and precipitating the amidosulphonic acid by the addition of a large excess of concentrated sulphuric acid. To get a large yield easily, the following details must be observed. Sodium nitrite (2 mols.) and sodium carbonate (3 mols.) are put into enough water to make the whole weigh 18 times as much as the sodium nitrite, and sulphur dioxide is passed in until the solution is acid to litmus. Usually the solution undergoes change very quickly if left to itself, but a drop of strong sulphuric acid may be added to start it, the nitrilosulphonate being converted into imidosulphonate and acid sulphate. There is a marked development of heat, and a large amount of sulphur dioxide is evolved, due to the interaction of the acid sulphate and sodium metasulphite, the latter salt having had to be produced in order to secure the sharp sulphonation of the nitrite (Trans., 1892, **61**, 955). Much of the loss of the sulphur dioxide, and also the inconvenience caused by its escape, can be easily avoided by distributing the nitrite solution in several flasks for separate sulphonation, and then allowing the sulphur dioxide regenerated by the hydrolysis of one portion to help in sulphonating another; in doing so, the sulphur dioxide may be driven out of the hydrolysed solution, without detriment to it, by heating, provided this is not too prolonged. In any case, either a short heating is requisite in order to hasten the second stage in the hydrolysis (that of imidosulphonate into amidosulphonate and acid sulphate), or else a setting aside of the solution for a few hours (after expelling its sulphur dioxide by a current of air) in order to allow this hydrolysis to become complete. The solution is next neutralised by adding 1 mol. sodium carbonate, that is, a third as much as the quantity taken at first, and the solution evaporated, by boiling or otherwise, until it again weighs only 18 times as much as the nitrite taken. If it is then exposed in an open vessel for a night, where the temperature may fall to 0° or below, nearly all the sulphate present will separate in large crystals, from which the mother liquor can be well drained. If these conditions are not observed, it becomes necessary to concentrate the mother liquor, and the sulphate, which then separates on cooling, seldom crystallises in so good a form for draining. It is worth while to redissolve the separated sodium sulphate in a third of its weight of hot water and recrystallise it, the mother liquor being then evaporated to one-fifth, cooled, and, after separation of the sulphate, added to the main quantity of mother liquor. The solution of sodium amidosulphonate, after being filtered, is now mixed with concentrated sulphuric acid, weighing 3—3½ times that of the nitrate taken, and set aside for a day in a cool place. Most of the amidosulphonic acid separates immediately; more crystallises out during the cooling and standing. It is well drained on porous tiles, and washed with a little ice-cold water.

The yield of acid by this process is affected by the tendency of the acid to form crystals with sodium hydrogen sulphate (see the account of the salts, p. 1646), so that the sodium sulphate should be separated as far as possible before adding the sulphuric acid. A yield of 75 per cent. of the calculated quantity may be reckoned on, while with care much more can be obtained.

To obtain the acid in good crystals, it must be purified by recrystallisation; this can be done without any considerable waste by grinding it fine, adding it to $2\frac{3}{4}$ times its weight of boiling hot water, and stirring diligently on a water bath until it is all dissolved. The solution set aside deposits about three-fifths of it, and the mother liquor by cold evaporation will yield nearly all the remainder in fine crystals in spite of the hydrolysis which the hot water will have caused. Mother liquors may also be worked up by precipitating the acid by means of strong sulphuric acid or by alcohol.*

Properties of the Acid.

Amidosulphonic acid is colourless and odourless, and has a sharp, purely acid taste (Berglund). It crystallises readily from its aqueous solution, and better than most of its salts (Berglund). Its crystals are orthorhombic plates; Fock (see Raschig's memoir) has examined it crystallographically, and shown it to be isomorphous with its potassium salt. We took its sp. gr. in ether, and found it to be 2·03 at 12°. Nothing has been published as to its melting point, except that M. Schmidt placed it as near 200°; it has, in fact, no real melting point, for, as will be shown later on in this paper (p. 1650 *et seq.*) in the act of melting it to a great extent decomposes. Its apparent melting point, as near probably as can be determined, is 205°, the observation being made on the driest acid in a capillary tube, beside a Jena thermometer with thread immersed in a bath of sulphuric acid; it melts but very slowly at this temperature. Even at its melting point, it begins to evolve vapours produced by its decomposition, but this is very slight in dry air. In fact, this volatilisation and the melting point are greatly affected by the access of moist air and by any dampness in the acid used.

Berglund described it as being quite easily soluble in water, and it is so, though slowly; it is, however, less soluble than any of its salts, except that of silver (not counting its basic mercury salt). It requires 5 parts of water at 0°, and $2\frac{1}{2}$ parts at 70° to dissolve it. The fact that hot water is not without chemical action on it ren-

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* For another, sometimes useful, way of preparing the acid, see p. 1646.

ders a close determination of its solubility in hot water impossible. There is no known solvent for it but water.

Sulphuric acid greatly diminishes the solubility of the acid in water, and readily precipitates it from its solutions and from solutions of its salts; its solubility is also greatly reduced by the presence of sodium hydrogen sulphate. These facts, as already mentioned, greatly facilitate the preparation of the acid. Not more than 3 parts of the acid for each 100 of water remain dissolved after concentrated sulphuric acid, amounting to $\frac{1}{5}$—$\frac{1}{4}$ of the volume of the solution has been added, and the mixture left to itself for a day. A 5 per cent. solution of the acid very soon deposited some of it when mixed with sulphuric acid; a $2\frac{1}{2}$ per cent. solution deposits none, even on standing, but if it has been previously nearly saturated with sodium hydrogen sulphate, it yields some of the acid on standing, after admixture with sulphuric acid. Nitric acid also precipitates amidosulphonic acid from its solution, but to a much less extent than sulphuric acid does. A fuming solution of hydrochloric acid does not precipitate it. Glacial acetic acid acts well as a precipitant, but more of it must be used than of sulphuric acid.

It is stable in the air (even when crude) and non-deliquescent in the cold, but it generally holds about 1 per cent. of water, either hygroscopically or, to a slight extent, as ammonium acid sulphate. It is also stable in cold solution (Berglund), or very nearly so. Neither dilute hydrochloric acid nor a mixture of this acid with barium chloride seem to affect its stability in the cold. A solution of the acid may be boiled for a moment, or be kept at 100° for a very few minutes, and still fail to show sulphuric acid with barium chloride; at 45° there is just enough hydrolysis in two hours to give a turbidity with barium chloride in 20 seconds. The presence of hydrochloric acid in a boiling solution quickens the destruction of the acid very much, but, even then, it is not completed in the course of a few hours; heating with the acid at 150°, however, makes the hydrolysis complete in three or four hours (Raschig).

Berglund stated that the acid in aqueous solution can be boiled for an hour without decomposition occurring, although continued boiling decomposes it; moreover, although hydrochloric acid hastens matters, the solution may be boiled with this acid and barium chloride for an hour before barium sulphate begins to separate. Raschig also stated that, in its boiling solution, the acid is practically undecomposed, and only very slowly decomposes in presence of acids. According to our experience, just recorded, Berglund and Raschig have exaggerated the stability of the acid in boiling solutions, whilst Krafft and Bourgeois, on the other hand, exaggerated still more its instability when, in purifying the acid, they only ventured to dissolve it in slightly warm water.

Crystals of the acid will lie for months in concentrated sulphuric acid unchanged; heated with it till dissolved, the acid undergoes essentially the same change as when heated by itself. Berglund found the acid not to be decomposed by boiling with potassium hydroxide; whilst, according to Raschig, alkalis seem to make the acid more unstable. We find the decomposition caused by continuous boiling to be very slight, and no greater than that in a solution of the neutral potassium salt kept at the same temperature. Alkalis appear, therefore, to be inactive. A solution of the potassium salt along with potassium hydroxide can be evaporated on the water bath, without the salt suffering noticeable change. Were it otherwise, how could sulphamide, boiled with alkali, produce amidosulphonate, half the nitrogen only escaping as ammonia (Traube)?

Heated in ordinary damp air at 100°, amidosulphonic acid very slowly fixes water, through hydrolysing, and becomes sticky on the surface of its crystals. Krafft and Bourgeois found this change to proceed freely at 130—140°. Berglund, on the contrary, found that the acid does not change in this way until above 190°; but the facts observed by Berglund are such as occur without the intervention of moisture, as will be made clear when the effects of heating the acid are described.

Amidosulphonic acid retards the precipitation of small quantities of sulphuric acid by barium chloride, a fact that must be taken into account when testing for the beginnings of decomposition of the acid itself. A cold saturated solution of amidosulphonic acid containing one part of sulphuric acid to 10,000 of water, gives no precipitate for some minutes after barium chloride solution is shaken with it, and then only slowly and sparingly, although in 20 hours precipitation seems to be nearly complete. With only half as much sulphuric acid present, barium chloride takes half an hour to cause any precipitate, and this remains very slight for a long time. In strong, neutral, or alkaline solutions, alkali amidosulphonates also retard, for a day or two, the complete precipitation of a sulphite by barium chloride.

Amidosulphonic acid, when acted on by sodium, changes into its sodium salt with evolution of hydrogen. It also dissolves zinc and iron (Berglund). It does not decompose an alkali chloride or nitrate when mixed with the salt in the damp state, or in solution. Heated dry with the salt, it causes decomposition, but then the acid is itself decomposed.

Amidosulphonic acid is decomposed with effervescence, even at the ordinary temperature, by a mixture of concentrated sulphuric acid and a nitrate or nitric acid, the gas being nitrous oxide. In this respect its behaviour is like that of imidosulphonic acid, which, in 1892, we fully described on p. 963 of our paper on "Imidosulphonates" (Trans., 1892, **61**). Soon after issuing that paper, we recognised the similarity of this reaction to that discovered by Franchimont (1887)—that by which nitramide has recently been obtained by Lachmann and Thiele (1896); but we were at that time unable to study the reaction further. Lachmann and Thiele have been the first to publish the fact that amidosulphonic acid gives nitrous oxide when treated with nitric and sulphuric acids. They also state that nitramide itself cannot be got by the reaction, but they give no particulars. We, too, have failed to get any nitramide, not, apparently, because it is decomposed after being formed, but because there is no action between the nitric and amidosulphonic acids in a freezing mixture. As already mentioned, amidosulphonic acid is quite insoluble in strong sulphuric acid, and but little soluble in the dilute acid. Owing to this property, we have been able to recover from a mixture of the acids, which had been stirred up for nearly an hour, immersed in ice and salt, not only much of the nitric acid (by ether extraction), but, also, much of the amidosulphonic acid, by getting it deposited when the mixed acids, holding it suspended, were poured on to ice to dilute them. In our experiment, we used the amidosulphonic acid in the form of its ammonium salt, with the object of having the acid present in the finest state of division.

As has just been indicated, amidosulphonic acid is oxidised in the cold by nitric acid in presence of concentrated sulphuric acid. It is also oxidised by hot, or even cold, nitric acid, by potassium chlorate and hydrochloric acid (Berglund), and by chlorine and bromine. It is not acted on by chromic acid or permanganic acid solution, or by ferric chloride, ferric amidosulphonate being as stable in hot solution as the other salts of the acid; the acid is slowly oxidised, however, at a boiling heat by silver oxide and alkali, and then silvers the glass. This oxidation gives the solution the power, when acidified, of reducing small quantities of permanganic acid. This property, together with the fact of sulphites in alkaline solution not being oxidisable by silver oxide, makes it pretty certain that the reduction of silver goes on thus (but see the account of the silver salt, p. 1648):

$$H_2NSO_3K + Ag_2O = AgSO_3K + Ag + N + OH_2.$$

Platinum black very slowly acts on a solution of amidosulphonic acid exposed to the air, and produces sulphuric acid—but, apparently, only by hydrolysis.

Amidosulphonic acid prevents the precipitation of silver and mercuric salts by alkalis (see the accounts of the silver and oxymercuric salts, pp. 1648, 1650). Here the acid is seen acting as an amine.

It combines with boiling alcohol in the course of hours, becoming ammonium ethyl sulphate (Krafft and Bourgeois), and, when boiled with aniline, it is slowly and similarly converted into ammonium phenylamidosulphonate (Paal and Kretschmer, 1894); both reactions are analogous to the hydration of the acid, NH and O functioning alike.

A description of its behaviour, when heated dry, will be found after the account of its salts.

Preparation and Properties of the Salts.

A number of the salts of amidosulphonic acid were examined by Berglund, and a comparatively full account of his work on them, condensed by Clève from Berglund's Swedish memoir, was published in the *Bull. Soc. Chim.*, **29**, 422. The salts examined were those of potassium, sodium, lithium, ammonium, thallium, silver, barium, strontium, calcium, lead, nickel, cobalt, manganese, zinc, cadmium, and copper, and the existence of a basic mercuric salt was pointed out. Raschig prepared again and analysed the potassium salt, and included, in his account of it, its crystallographic elements, as determined by Fock. Krafft and Bourgeois again analysed and described the barium salt. Eitner again analysed the barium and the silver salts. Paal and Kretschmer again analysed and described the silver salt (acknowledging the previous work of Eitner), the copper salt, and the lead salt. Of these investigators, Raschig alone mentions Berglund, carefully indicating the great value of his work. The others are silent as to the work of the chemist who not only first prepared the acid and its salts, but analysed and described them at least as fully as they have done. Yet an epitome of Berglund's paper, drawn up by himself, appeared in the *Berichte* of the German Society (and not among the *Referate*), besides appearing, in another form, in the *Bulletin* of the French Society, as we have just said.

Now that the isolation of the acid has become easier than that of any of its salts, the work of Berglund and of Raschig on the preparation of the salts has lost its value. Berglund, by laborious processes, prepared the barium salt by hydrolysing either the barium or the mercury barium imidosulphonate, and from this obtained the acid and the other salts. He gave himself unnecessary trouble through his belief, founded on observation, that imidosulphonates have a great tendency to pass at once into ammonium sulphate, instead of stopping at the stage of amidosulphonates, although these, once formed, are stable enough. Instead of describing Berglund's, now obsolete, process, we will give a very simple modification of it that may sometimes prove useful. Normal barium imidosulphonate, freed from alkali by reprecipitation, is kept on the water bath, with very slightly more dilute sulphuric acid than is equivalent to one-third of its barium, just so long as a little of the filtered solution is found to yield barium sulphate on boiling; then, after filtering off and washing the barium sulphate, the solution of amidosulphonic acid is evaporated in the cold over sulphuric acid.

Nothing need be said of the preparation of the salts from the acid, but a line or two may be given to the direct preparation of the sodium and potassium salts from the nitrite. If, in the preparation of the acid from sodium nitrite already described, the mother liquor from the sodium sulphate crystals is further evaporated, sodium amidosulphonate crystallises out, and can be thus obtained, but it is far better to prepare the salt from purified acid and sodium carbonate. Raschig obtained the potassium salt direct, in the above way. Other amidosulphonates cannot be prepared by double decomposition of the alkali salts (see the account of the silver salt, p. 1648).

All amidosulphonates (except the oxymercuric) are soluble in water, the least soluble of them being the silver salt (Berglund). Most of them are exceedingly soluble, and form supersaturated solutions (Berglund). They are stable, even in solution, so far as we have observed, except the ammonium salt, which is liable to hydrolyse, if not quite dry, moreover, their solutions may be kept for hours at 100°, or even be boiled without showing decomposition.

A double salt of sodium sulphate and amidosulphonic acid has been obtained by us at times, when preparing amidosulphonic acid and separating it from its sodium salt by sulphuric acid; but experiments made to determine the conditions for its production at will have been unsuccessful. When obtained by us, it had crystallised from a strongly acid solution, and formed short, thick prisms, somewhat deliquescent. Its analysis showed it to have the composition of 6 mols. amidosulphonic acid with 5 mols. disodium sulphate, and 15 mols. water.

	Calc.	Found.
Sodium	14·72	14·79
Sulphate sulphur......	10·24	10·18
Sulphonate sulphur....	12·29	12·08
Water	17·28	15·70

This complex may have been only a crystal compound, but it could not have been a mere mixture, because of its form, its apparent homogeneity, and its content of water. It may be written as $H_2N{\cdot}SO_3H + 5(NaO{\cdot}SO_2{\cdot}NH_2{\cdot}HO{\cdot}SO_2{\cdot}ONa,3OH_2)$, which, if the

1 mol. of amidosulphonic acid be neglected, is a salt analogous to the well defined and stable ammonium sodium sulphate formed under similar circumstances, the sodium amidosulphonate representing ammonia. In our accounts of imidosulphonates and oximidosulphonates, already published, we have had occasion to point out the apparent functioning of those salts as amines towards nitric acid.

Hydroxylamine amidosulphonate has only been obtained as an uncrystallisable, viscous, hygroscopic liquid. It was prepared by decomposing hydroxylamine sulphate by its equivalent of barium amidosulphonate.

Ferrous Amidosulphonate.—This salt was prepared from the acid and iron wire, with exclusion of air. Since the solution of this very soluble salt has to be evaporated in a vacuum, it is well to use much less water than would dissolve all the acid, for this then goes into solution in proportion as it is used up in forming the iron salt. The solution and crystals have the usual blue-green colour. The solution shows supersaturation, like that of many other amidosulphonates, and the salt is consequently obtained in the form of a cake of radiating prisms, just like the zinc salt. It is deliquescent, and, unlike the sulphate, is not precipitated by alcohol. Pressed between filter-paper, but still slightly damp, some of the salt showed, by permanganate, the presence of 16·48 per cent. of iron. A salt with $4H_2O$ would have 17·5 per cent. of iron, and one with $5H_2O$, 16·57 per cent.; the latter must, we think, be taken as the right expression. Analogy is not available for deciding the point, for, according to Berglund, although the zinc salt has $4H_2O$, the nickel, cobalt, and manganese salts have $3H_2O$, the cadmium salt $5H_2O$, and the copper salt $2H_2O$. The magnesium salt has not been prepared.

Ferric Amidosulphonate.—This salt was prepared by dissolving ferric hydroxide and the acid in water. Its solution is bright brown, and dries up into an opaque, amorphous, brittle mass of the colour of ferric hydroxide. It is very soluble in water, but is not at all deliquescent. It has the full, astringent taste of the ferric salts of inorganic acids, and not that of the citrate or tartrate.

The Silver Salt.—Before passing to the results of our own examination of the important silver salt, we give Berglund's excellent account of it. "It crystallises best of all the salts; it is also the least soluble, requiring about 15 parts of water at the ordinary temperature (19°). It forms bundles of striated prisms, looking much like those of the sodium salt, and almost as hard and brittle as glass. It blackens only extremely slowly; its solution is quite neutral. It is best prepared from barium amidosulphonate and a solution in boiling water of its equivalent of silver sulphate." (Then follows its analysis, showing it to be anhydrous). It is, however, better to prepare it directly from the acid itself.

It is noteworthy that silver amidosulphonate cannot be prepared from the potassium salt and silver nitrate, as the most concentrated solutions of these salts, mixed in molecular proportions, yield no crystals; when dried up in the desiccator, it leaves a mixture of crystals consisting of silver amidosulphonate in combination, apparently, with silver nitrate, of potassium nitrate, and of silver potassium amidosulphonate nitrate.

On adding potassium hydroxide to a solution of the silver salt, not too dilute, a bright yellow-ochre precipitate is produced, and if the potassium hydroxide is in moderate excess, the mother liquor is bright yellow, like a solution of gold chloride. Both precipitate and solution are changed by much water, becoming brown, the precipitate dissolving. Either solution, gives a brown precipitate when heated, or when mixed with excess of potassium hydroxide, of silver nitrate, or of potassium amidosulphonate, and this precipitate cannot be redissolved. The yellow solution is also unstable, gelatinising on long standing, and becomes colourless. The yellow and brown precipitates and solutions appear all to be colloïdal in character. The brown substance in solution and the brown precipitate appear to be essentially silver oxide. The yellow compound is not blackened by light, is soluble without colour in potassium amidosulphonate, is slowly converted to a whitish, pulverulent precipitate by digestion with silver nitrate solution, and into a white flocculent precipitate by excess of potassium hydroxide. Its solution in a minimum of potassium amidosulphonate silvers glass at a boiling heat, so does a solution of potassium amidosulphonate, silver nitrate, and potassium hydroxide.

A solution of silver amidosulphonate does not sensibly dissolve silver oxide. A solution containing silver nitrate and its equivalent of potassium amidosulphonate behaves towards potassium hydroxide like silver amidosulphonate. If the silver nitrate is present in excess, and the solution not too dilute, precipitation of the amidosulphonic compound precedes that of silver oxide, but if the proportion of potassium amidosulphonate is as 2 mols. to 1 of the silver nitrate, potassium hydroxide causes no precipitate in solutions of moderate concentration, that is to say, amidosulphonic acid prevents the precipitation of silver oxide by alkalis. A solution of 2 mols. of potassium amidosulphonate, 2 mols. of potassium hydroxide, and 1 mol. of silver nitrate dries up in the desiccator to a white homogeneous mass of minute, silky fibres, soluble in water again without change. Alcohol extracts from it no notable quantity of potassium hydroxide.

Further experiments are necessary to justify us in speaking positively, and these, for the time, are impossible, but there can be little doubt, from what has been already ascertained and from analogous facts, that one of the amido-hydrogens is replaceable by silver, and even by potassium; that the ochre-yellow colloïdal substance, soluble in water (when it is neither too much nor too little), is $AgHNSO_3K$; and that the white, fibrous, very soluble salt is a compound of silver potassium amidosulphonate with dipotassium amidosulphonate, ($KHNSO_3K$), and potassium nitrate. The power of preventing the precipitation of silver salts by alkalis exhibits amidosulphonic acid playing the part of an amine. It has no solvent effect in the case of cupric salts; in that of cuprous salts, its action has not yet been tried. The reduction of silver by amidosulphonic acid has been already briefly discussed along with the other properties of the acid (p. 1644).

Mercurous amidosulphonate cannot exist. With a solution of mercurous nitrate, the acid gives a precipitate of metallic mercury and the salt next described.

Oxymercuric Amidosulphonate.—Berglund recorded that silver amidosulphonate, with mercuric chloride, gives a mixed precipitate of silver chloride and basic mercuric amidosulphonate, amidosulphonic acid being set free. The normal salt cannot be obtained. When mercuric oxide and amidosulphonic acid are ground together and moistened, they slowly interact, so that, with occasional stirring, the action is complete in two or three days, but the oxymercuric salt, $(H_2NSO_3HgO)_2Hg,2H_2O$, alone is formed, any excess of acid dissolving out in water, without taking any mercury with it, and any excess of mercuric oxide, evident by its red colour, being removable by digestion with much diluted nitric acid. Mercuric chloride and potassium amidosulphonate mix together in solution without change, but, if the former is not in excess, the above-mentioned salt is obtained as a white precipitate on adding potassium hydroxide in quantity not exceeding the equivalent of the chloride. The acid can precipitate almost all the mercury from a solution of mercuric nitrate, leaving only nitric acid in solution, and is itself completely precipitated by a slight excess of mercuric nitrate.

To prepare the salt, it is best to mix a dilute solution of the acid with a concentrated solution of mercuric nitrate in the minimum of nitric acid, when the salt is thrown down as a snow-white, voluminous, and very finely divided precipitate, which is troublesome to wash, either by decantation or on the filter, and takes long to dry on a tile, in consequence of its fine state of division. It is very stable, and may be washed with hot water. Air-dried, at the common temperature, it contains $2H_2O$, which it easily loses when heated at 115°. The results of its analysis are as follows:

	Mercury.	Sulphur.	Water.
Calculated	69·77	7·44	4·19
Found	70·80	7·49	4·65

The mercury found is too high through imperfect determination, for when the calculation is made, the total a little exceeds 100; the error does not affect the formula adopted.

The salt requires comparatively strong nitric acid to dissolve it in the cold. Hydrochloric acid dissolves it, of course; but, what is very remarkable, potassium hydroxide does so too. By using an insufficient quantity of alkali, it is possible to decompose the salt partly, and thus to get a little yellow mercuric oxide from it, which remains insoluble in excess of alkali; but when the alkali, in excess, is rapidly mixed with it, the salt all dissolves permanently. Mercuric chloride, in presence of enough amidosulphonic acid, is not, therefore, precipitated by potassium hydroxide in excess; the addition of more mercuric chloride, or of a little acid, causes the white oxymercuric salt to precipitate, but not mercuric oxide.

The precipitation of the oxymercuric salt from an acid solution of mercuric nitrate indicates its nature as a basic salt, while in degree of basicity it agrees with the oxymercuric salts of sulphuric, sulphurous, and imidosulphonic acids, that is, it contains the bivalent group, $-OHgOHgO-$. But the stability of the salt when heated, its insolubility in dilute nitric acid, and its solubility in an alkali, suggest the possibility of its having another constitution, or of its being subject to tautomery. At least in its alkaline solution, it must almost certainly exist as a potassium salt of the formula $Hg''_3N_2(SO_3K)_2(OH)_2$, which exhibits it as a sulphonated mercurammonium hydroxide. Like other mercurammonium salts, it does not yield up its amine (amidosulphonic acid) when treated with alkalis. It also behaves like a mercurammonium compound, in being completely resolved, in accordance with Pesci's reaction, into amidosulphonic acid (its amine) and mercuric bromide by a saturated solution of ammonium bromide, ammonia being liberated, thus:

$$Hg_3N_2(SO_3H)_2(OH)_2 + 12NH_4Br = 3[HgBr_2(NH_4Br)_2] + 2NH_2SO_3NH_4 + 4NH_3 + 2H_2O$$

Dilute solution of ammonium chloride converts it into "white precipitate," and a solution of mercury ammonium chloride and ammonium amidosulphonate, without any ammonia being liberated.

Effect of heating Amidosulphonic acid and its Salts.

The only statement yet made, concerning the effect of heating amidosulphonic acid in the absence of water, is Berglund's, that, when rapidly heated, it is decomposed; sulphur dioxide, nitrogen, water, and sulphuric acid being produced. This is correct, although it is remarkable that ammonia is not mentioned, as it always occurs in combination among the products. But, much below the temperature at which the acid is converted into these products, it suffers a complete chemical change; this occurs to a large extent at the temperature at which the acid appears to melt, that is at 205°. In a closely limited space, to which air has not free access, it sustains no loss in half an hour when heated to 220°, and only about 1 per cent. when heated to 260°; just above 260° small bubbles very slowly form in the liquid, but become reabsorbed if the temperature is lowered; they consist, almost certainly, of ammonia. There is much expansion in the act of melting, the unmelted particles sinking freely in the melted part; on cooling, the liquid forms a vitreous mass, which contracts so much as to partly detach itself from the glass, even cracking this when very thin. The vitreous product is brittle, exceedingly deliquescent, and very soluble in water. If kept dry, it remains quite transparent, and shows no tendency to crystallise even after the lapse of several days.

Although the vitreous mass obtained by fusing the acid must have the same ultimate composition as the acid itself, it yet contains very little of that acid; for when the mass is dissolved in water more than half the acid that has been fused appears as ammonium hydrogen sulphate, that is, has combined with the elements of water. Now as it is plainly impossible that the change into this substance could arise from the effect of heat alone, it must necessarily be in part, at least, due to the action of water when the mass is dissolved. This can easily be shown to be the fact, but in doing so it becomes established that nearly half the acid is actually converted into sulphate by heat alone. When the mass is dissolved in a solution of potassium hydroxide instead of in water, sulphuric acid and ammonia are still the principal products, but the proportion of the former is now not so great as before. In the alkaline solution, imidosulphonate is present in large quantity, sometimes separating out from it in crystals. Since the quantity of ammonia is the same whether the mass is dissolved in presence of potassium hydroxide or not, and since the quantity is more than would be required to form sulphate with the sulphuric acid present in the alkaline solution, it follows that some of the ammonia must exist in the vitreous mass as ammonium imidosulphonate. This explains how it is that more sulphuric acid is got by dissolving the fused product in water than when alkali is present, as the acid imidosulphonate very rapidly hydrolyses into sulphate and amidosulphonic acid. Accordingly, the solution in water contains nothing but ammonium hydrogen sulphate and amidosulphonic acid; whilst, in the alkaline solution most of the sulphur may be present as sulphate and imidosulphonate and very little as amidosulphonic acid. From this it is evident that in the production of ammonium sulphate by heat alone, one part of the acid must yield the elements of water to the other part, being itself converted into imidosulphonate, for nothing escapes during the heating. This is only possible if both sulphate and imidosulphonate come into existence as their pyro-salts; and although neither of these is yet known or has been isolated from the vitreous mass, the analytical data point to the presence in it of these two pyro-salts in molecular proportion, along with some unchanged amidosulphonic acid. The following equation expresses the formation of the pyro-salts:

$$4H_2NSO_3H = (NH_4SO_3)_2O + NH_4N(SO_2)_2O.$$

The formation of acid imidosulphonate,—

$$4H_2NSO_3H = 2NH_4N(SO_3H)_2,$$

and that of pyrosulphate,—

$$4H_2NSO_3H = (NH_4SO_3)_2O + (H_2NSO_2)_2O,$$

are not necessarily simultaneous; but, within the limits of analytical determination, they appear to be so. In the case of some amidosulphonates, however, the conversion to imidosulphonate partly precedes that into sulphate.

On heating the acid much above 260°, the products first formed enter into decomposition. The vapours evolved at first are dense white, and apparently contain much sulphur trioxide, besides dioxide diluted with much nitrogen; but as the temperature rises and decomposition gets more rapid, the vapours become almost transparent. The decomposition induced by this higher heating is an interesting sequel to the primary decomposition of the acid by heat, the pyro-salts becoming ordinary salts in the following way, as closely as can be traced:

$$5(NH_4SO_3)_2O + 5NH_4N(SO_2)_2O = 6NH_4HSO_4 + 3HN(SO_3NH_4)_2 + 2N_2 + NH_3 + 6SO_2 + 2SO_3.$$

When this change is about complete, the decomposition, at still higher temperatures, goes on in such a way as to preserve a residue nearly steady in composition as regards sulphur (29 per cent.), but to cause it to become richer in water and poorer in ammonia and imidosulphonate, until, quite at the last, the residue consists of ammonium hydrogen sulphate alone.

The Salts.—When the amidosulphonates of ammonium and potassium, are carefully heated, they give a very large proportion of the corresponding imidosulphonates. The barium salt under the same circumstances gives much two-thirds normal ammonium imidosulphonate and an orange-coloured sublimate of nitrogen sulphide.

The silver salt is first converted into an imidosulphonate, $NH_4N(SO_3Ag)_2$, and this, at a higher temperature, loses ammonia and appears to be changed into $HN(SO_3Ag)_2$.

The oxymercuric salt does not decompose until heated nearly to redness, when it gives off sulphur dioxide and nitrogen, whilst at a red heat much mercury, as well as mercury sulphates, volatilise. In the remarks which follow, the mercury salt is not taken into consideration, its decomposition being specific.

Summary of the Effects of heating the Acid and its Salts.—Varied as are the details of the decomposition of amidosulphonates by heat, according as they concern the acid or its barium salt, the ammonium or the potassium salt, the characteristics of the decomposition are the same. There is always, virtually, the change of 2 mols. of amidosulphonate into imidosulphonate and ammonia, and, for the most part, the union of these to form a normal salt,

$$2H_2NSO_3H = NH_3 + HN(SO_3H)_2;$$
$$(H_2NSO_3)_2Ba = NH_3 + HN(SO_3)_2Ba.$$

That change is the cumulative resolution of an amine; next comes the cumulative resolution of the imidosulphonate as a hydroxide or metalloxide. The elements of 1 mol. of water and, in the case of metal salts, 1 mol. of basic oxide, go from 1 mol. of the imidosulphonate to another mol. of it, converting this into sulphate, pyro or normal, as the case may be, and leaving either pyro-imidosulphonate as a residue, or (when basic oxide has been also lost) nitrogen, ammonia, and sulphur dioxide, as representatives of what, at lower temperatures, might have been sulphimide,

$$2NH_4N(SO_3H)_2 = (NH_4SO_3)_2O + NH_4N(SO_2)_2O;$$
$$2NH_4N(SO_3)_2Ba = 2BaSO_4 + 2NH_3 + [2HNSO_2].$$

The complex $[2HNSO_2]$ appears as $\frac{2}{3}(NH_3 + N_2 + 3SO_2)$, or, in the case of the barium salt (infusible as that is, and acquiring a higher temperature as it does) this complex partly interacts with the $2NH_3$, according to the equation

$$2NH_3 + 2HNSO_2 = 4H_2O + 2NS + N_2.$$

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