Oximidosulphonates or Sulphazotates.

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By treating a solution of potassium nitrite and hydroxide with sulphur dioxide, Fremy, in 1845, discovered a series of salts of complex composition, of which, without succeeding in getting any definite insight into their chemical constitution, he was yet able to indicate to some extent a classification into three groups: the *sulphazates*, the *sulphazotates*, and the *sulphammonate*. He attached, and justly so, special importance to the sulphazotates, the salts which are the subject of the present paper, and from which by hydrolysis are derived the *oxyamidosulphonates* treated of in an earlier communication by us to this Journal (**3**, 211, where will be found references to the papers of Fremy, Claus, and Raschig, which will serve for the present paper).

A slight difference in procedure gave Fremy one or other of two salts, which he named respectively *basic sulphazotate* and *neutral sulphazotate*, because from their chemical composition and their ready passage into each other he held them to be salts of the same acid. He also described still more basic sulphazotates of potassium with barium and with lead.

Claus in 1871 worked upon the two sulphazotates, and gave an account very different from Fremy's of their composition, properties, and relations to each other. Finding them inconvertible into each other, he referred them to different acids and renamed them. He brought to light the sulphonic constitution of these salts (which had been, however, foreshadowed by Fremy), and consequently named the *neutral* sulphazotate of Fremy *disulphydroxyazate*, while for the latter's *basic* sulphazotate he retained the name *sulphazotate* simply.

The sulphazotates were again examined in 1887 by Raschig, who established their constitution as derivatives of hydroxylamine* and made discovery of a potassium salt still more alkaline than Fremy's *basic* salt. He, in his turn, differed greatly from Claus and found Fremy's account of the salts in some respects more in accordance with the facts, but, on other grounds than those Claus had taken, retained the distinction made by this chemist between the neutral sulphazotate, which he renamed *hydroxylamine-disulphonate*, and the basic sulphazotate, which he agreed with Claus in calling simply *sulphazotate.* To his own discovered third potassium salt he gave the name of *basic sulphazotate.*

In the present contribution to the subject the existence of *sodium* oximidosulphonates is established; these and salts of ammonium, calcium, strontium, barium, and lead are described; much-needed methods, definite and productive, for preparing both sodium and potassium oximidosulphonates are given; the reversion of these salts to sulphite and nitrite made known; and the interrelations of the salts

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* Claus had pointed out the hydroxylamine derivation of oxyamidosulphonates but had decided against such a derivation for the (neutral) sulphazotate. In a foot-note to our preliminary paper on the *Reaction between sulphites and nitrites*, *J. Ch. S.* **51**, 659, we erroneously represented Raschig to be not quite accurate in stating that Claus had so decided. We regret our error. The facts are that while in one place, overlooked by us, in his several long papers Claus expressly makes this decision, he in another place, indicated in our note, gives the formulæ—$ONH(SO_3K)_2$ and $HON(SO_3K)_2$—as alternative, without deciding between them.

classed apart by Claus and by Raschig shown to be such as to demonstrate the unity of their constitution as oximidosulphonates, or Fremy's sulphazotates.

Preparation of sodium and potassium oximidosulphonates.

In practice two courses are open by which to proceed in preparing oximidosulphonates from nitrites: * to mix together solutions of the nitrite and sulphite; and to treat a solution of the nitrite and hydroxide or carbonate with sulphur dioxide. The question, already discussed by Claus, whether these methods are in principle identical, need not here be considered, and will be taken up in a future paper.

Fremy succeeded only by the second of these methods in getting oximidosulphonates. Claus found both successful but the second to be much more productive. Raschig recommended (*Annalen*, **241**) the first method as being the more convenient and productive when sodium salts are worked with, neutral potassium oximidosulphonate and also an alkaline potassium-sodium oximidosulphonate being then got by double decomposition with potassium chloride. Only incidentally, in discussing Claus's views, did he mention that the second method of getting the potassium oximidosulphonates is occasionally successful. He included, however, this method in the specification of his patent (1887)** for the manufacture of hydroxylamine. Both methods have been investigated by us, and in what follows it will be seen that we have found the second method to be much the better one, whether for the potassium or for the sodium salt, but that the first can be made far more successful than it has hitherto proved to be.

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* It has been shown by Raschig that oximidosulphonates are also obtainable from nitric oxide, namely, by first converting it into nitrososulphonate, Pélouze's salt, and then letting this decompose in alkaline solution.

** Our references concerning the patent are abstracts in the *Berichte*, *J. Ch. S.*, and *J. S. Ch. Ind.*

Oximidosulphonates prepared by the direct use of sulphite.

Introduction.—Claus supposed himself to use the normal or dipotassium sulphite but, it is clearly evident, used in reality mainly the metasulphite. The 'neutral' (or meta) sulphite therefore is to be taken in the proportion of 'less than four' molecules, or 2 $K_2S_2O_5$, to one of the nitrite, KNO_2; with more than four molecules only nitrilosulphonate—$N(SO_3K)_3$—separates, and even with less than four much of this salt is produced; both salts are almost insoluble, but the loose fine needles of the nitrile can be mechanically washed away from the large crystals of the oximide; the solutions used are not to be too dilute; the yield of oximidosulphonate is very small. We can confirm Claus's account of this very unproductive process.

To prepare the neutral salt Raschig runs into a mixture of the solution of one molecular proportion of sodium nitrite with ice, a solution of two molecular proportions of sodium disulphite (*i. e.*, one mol. of metasulphite), adds two molecules of potassium chloride in cold saturated solution, and leaves the whole to crystallise. Nitrile forms, as well as oximide, and the two salts are to be separated by elutriation, as directed by Claus. The yield of potassium salt is stated to be about half the calculated quantity. No mention is made in the memoir in the *Annalen*, or in the papers in the *Berichte*, of a similar proceeding with potassium nitrite and sulphite to get the potassium oximidosulphonate direct, the above indirect process obviously being resorted to as superior to it. But in the specification for the patent, which of course preceded the publication of the memoir, Raschig did give the direct method. His process has proved successful in our hands but less so than in his.

The same investigator records the preparation, from sulphite, of a potassium-sodium oximidosulphonate having the basicity of Fremy's basic potassium sulphazotate. Having on one occasion poured commercial solution of sodium bisulphite upon cold sodium nitrite he found the mixture become boiling hot, and by addition of much potassium chloride to yield much potassium-sodium nitrilosulphonate. Then, during the twenty four hours following, the mother-liquor deposited the new salt together with some potassium nitrilosulphonate. We have not been able to confirm his experience. The potassium-sodium salts we can get, but according to our own observation, the addition of alkali hydroxide, of which he says nothing, is requisite to form an alkaline oximidosulphonate. And from Raschig's own sound criticism (*op. cit.*, p. 222) of Claus's method of getting the alkaline potassium salt, it might be supposed that he too believed in this necessity of adding hydroxide in order to form any basic oximide.

Preparation of the neutral potassium oximidosulphonate from metasulphite.—To prepare the potassium oximidosulphonate by using metasulphite we ourselves work from the first with potassium salts. The solutions of potassium nitrite and metasulphite are used with ice floating in them, the mixture is kept in ice for a day or more, and the ice-cold mother-liquor is then drained off from the crystals which will have formed. To allow, as Raschig would, as we understand from abstracts of the specification of his patent, the temperature to rise even up to 40°, greatly interferes, and gives such a result as Claus obtained,—very much nitrile and very little oximide. Some nitrile forms even in the ice-cold mixture and has to be washed away from the oximide crystals ; and when the mother-liquor is afterwards allowed to acquire the common temperature it produces and deposits more nitrile.

The proportion of the quantities of the salts to be taken is somewhat more than that of three molecules of metasulphite to two molecules of nitrite, instead of one to one as when Raschig's directions are followed. In the mother-liquor remains much sulphite but only insignificant quantities, at most, of nitrite. In order to measure with some degree of accuracy the quantities of nitrite and metasulphite taken, it is best to use good commercial nitrite, the real strength of which in this salt is known from a previous assay ; and to prepare the metasulphite, shortly before it is wanted, by passing-in sulphur dioxide just to the point when the solution becomes neutral to methyl-orange or to lacmoïd paper. Some inconvenience in preparing the ice-cold solutions is caused by the sparing solubility of the metasulphite, which entails the cooling of large volumes of solution. The yield of washed crystals of the oximide is about 60 (63) per cent. of the calculated quantity, and such therefore as seems not to have been even remotely approached by previous workers, although greatly surpassed by that of the sulphur-dioxide method described on pp. 27 *et seq.* By working at temperatures some degrees below 0° the production of nitrile seems to be further lessened and that of oximide somewhat increased.

It is besides almost certain that the formation of the nitrile increases relatively to that of the oximide as the nitrite remaining grows less, the sulphite having more and more already-formed oximide to work upon along with less and less nitrite. This view of the matter is supported by experience. For when the metasulphite is added to an excess of nitrite, the crystals of oximide produced amount, when washed from the little nitrile accompanying them, to 80 per cent. of the quantity theoretically possible from the quantity of metasulphite taken.

Formation of the neutral sodium oximidosulphonate from metasulphite.—By treating one molecule of sodium nitrite with two, or a little less than two, of sodium metasulphite, the nitrite may be wholly sulphonated, principally into oximide but partly into nitrile. To prevent heating up the solutions are best mixed ice-cold, but the mixture may then be exposed to the ordinary temperature and left so for a day. This process though successful is of little practical value because the very soluble sodium oximidosulphonate cannot be separated from the sulphite and nitrilosulphonate which accompany it. The actual success of the process in forming much oximidosulphonate has been ascertained therefore only by analysis : the excess of sulphite having been precipitated as barium salt, the solution has been hydrolysed, and the hydroxylamine estimated. In this way evidence has been got that there is formed about 83 per cent. of the oximidosulphonate equivalent to the nitrite.

The solution of the sodium salt thus obtained can be used to get the potassium salt by double decomposition, like that prepared after Raschig's directions, than which it is markedly more productive and gives a purer product. Raschig used only half as much metasulphite as we use and therefore, by our finding, left one-third of the nitrite undecomposed in the solution. He also added the potassium chloride just after mixing the sodium salts, and did not, it would seem, preserve the coldness of the solutions necessary in presence of potassium salts. By his method, consequently, much more nitrile is got than by ours, in which the solution of the sodium salts is only treated with the potassium chloride after it has stood a day, so as nearly to complete the reaction, and then been cooled again in ice, to prevent as much as possible the formation of nitrile which otherwise goes on, especially in the potassium salt. Following this method the oximide is obtained with so little nitrile accompanying it as only to become visible during recrystallisation of the product. But these points are now of no importance as regards the preparation of the potassium salt, since there are according to our experience, the much better direct processes for its preparation, one just given (p. 19) and the other now to follow (p. 27).

Oximidosulphonates prepared by the use of sulphur-dioxide.

Introduction.—Fremy's process for the *neutral* potassium salt is to pass sulphur dioxide into a suitably concentrated solution of potassium nitrite and hydroxide, until the salt separates. Should the solution, however, be sufficiently concentrated, the *basic* oximidosulphonate will make its appearance instead, he found ; and with high concentration the *sulphazate*, and occasionally the *metasulphazate* will first form. Then water must be added, enough to dissolve up any of these salts, and the passage of sulphur dioxide be continued until the neutral salt begins to crystallise.

Claus found Fremy's prescription too indefinite and uncertain, and therefore modified it, mainly so far as to employ equivalent quantities of nitrite and hydroxide. He could get no such simple succession of salts as Fremy had obtained, and he had always much nitrile to deal with, a salt which gave no trouble to Fremy. Keeping the mixture cool during the entry of the sulphur dioxide, he got a solution which, not immediately, as Fremy had found, but only on standing, gave crystals of the neutral oximidosulphonate. Letting the mixture grow hot by the action of the sulphur dioxide, crystals separated, very much like Fremy's sulphazate, and these treated with enough water left much insoluble nitrile and gave a solution which slowly deposited crystals of the neutral oximide along with those of the basic oximide.

Raschig, in the specification of his patent, appends to the account of the process he gives for the preparation of the neutral oximidosulphonate a statement to the effect that this may also be obtained by passing sulphur dioxide in excess into a solution of alkali nitrite and its equivalent of either hydroxide or carbonate. But in his memoir in the *Annalen*, published later, he makes no mention of this, and condemns Fremy's and Claus's similar processes as being frequently unproductive, although Claus had also used equivalent quantities of nitrite and hydroxide. Evidently he thought little of this method because of its uncertainty; yet, as we shall show, it is, when properly modified, regularly very productive in the case of both sodium and potassium salts, and indeed is the only one by which sodium oximidosulphonate can be isolated.

Fremy prepared his *basic* salt nearly in the same way as his neutral salt, varying this only to the extent of working with more concentrated solutions, and so regulating the passage of sulphur dioxide (assisted, it would seem, by addition of more potassium hydroxide), that separation of crystals should take place with the solution still strongly alkaline. Some care was required as to the degree of concentration, which he adjusted by beginning with solutions strong enough to deposit sulphazate, and then adding just sufficient water to redissolve this before passing in more sulphur dioxide. The yield of salt was large. A secondary method of his was to make sulphazate and salts allied to it and then treat these with water, when the alkaline oximidosulphonate slowly crystallised from their solution.

Claus in following Fremy's main process could get the alkaline salt only in admixture with the neutral salt and other compounds. By fractional crystallisation it could indeed be separated from these, but he preferred a modification of Fremy's secondary process, in which salts nearly the same as Fremy's sulphazate, with their adhering alkaline mother-liquor, are boiled with two or three times their volume of water, the solution filtered hot, and when barely cold decanted from the crystals that have formed of the basic salt. This Fremy-Claus process is no longer, we consider, of any value, the two alkaline salts being readily obtainable from the neutral salt.

Preparation of the neutral sodium oximidosulphonate by the sulphur-dioxide method.—The salts are to be in the proportion of two molecules of sodium nitrite to one of sodium carbonate or to two of sodium hydroxide, but with about a tenth extra of the carbonate or hydroxide, (called for by the unavoidable* conversion of about a tenth of the nitrite into nitrile). In our experience this proportion gives about the highest yield of oximide along with decomposition of all the nitrite. Suppose the nitrite used to be 96 per cent. pure, and the quantity taken 50 grams. Then this is put with 110 grams of sodium carbonate crystals, or 30.8 grams of real sodium hydroxide, a piece of lacmoïd paper, and 150 cub. cents. of water when carbonate is taken, or 200 cub. cents. when hydroxide is taken, into a 500 cub. cents. flask, fitted with cork carrying inlet and exit tubes and, if convenient, a thermometer. The inlet tube dipping into the solution is connected with the sulphur-dioxide apparatus, and the exit tube with a washing bottle of water, by caoutchouc tubes of adequate length to allow of free movement of the flask. The stream of sulphur dioxide may be rapid (in the case of the carbonate being used, very rapid), but not so as to cause any fumes either white or red in the flask kept in active motion and immersed in water with ice floating in it. Hardly any sulphur dioxide at all will escape consumption. In about 70 minutes the solution will have become acid or nearly so, if the sulphur dioxide have been passed in at a good rate. Notice of the remote approach of neutralisation of the solution is given, when carbonate is being used, by the disappearance of the last of the sodium hydrogen carbonate which has been precipitated previously by the sulphur dioxide and, when sodium hydroxide has been used, by the disap-

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* No longer unavoidable; March, 1894.

pearance of the precipitated sulphite. By effecting neutralisation very slowly at the last until acidity to lacmoïd paper is just reached, the finish of the process may be so hit off that the solution is left free not only from nitrite but also from more than traces of sulphite. In practice we find it better to enter the gas quickly up to distinct acidity and then at once to stop its flow, for although the solution is then found to contain a not inconsiderable quantity of sulphite and to give off a small quantity of nitrous fumes, this hardly affects the yield of oximide, and there is great saving of time and attention. When the method of slow finishing has been followed it is usually necessary to add a drop of dilute sulphuric acid at last, to destroy nitrile.

In the solution, either way prepared, the nitrile present now suffers hydrolysis into imidosulphonate and acid sulphate. To make sure of the disappearance of every trace of this very unstable and therefore injurious salt, the solution is well cooled after the rapidly occurring hydrolysis, and left in its acid condition for ten or fifteen minutes, while in the case of its containing sulphur dioxide a free stream of air is blown through it to carry this away. For fifteen minutes or so in such a solution, the oximidosulphonate proves able to resist the hydrolysing action of a little sulphuric acid. To the solution deprived of all nitrile and almost all sulphur dioxide, concentrated solution of sodium carbonate is added until alkalinity is reached. For this purpose about 10 grams of the carbonate will be wanted but more should be at hand to at once arrest hydrolysis should it happen to have set up in the oximide.

The liquor is now a solution of about 150 grams oximidosulphonate in about 220 grams of water, along with 15 grams of disodium imidosulphonate, and 22 of hydrated sodium sulphate. After filtration from any impurities derived from the nitrite it has to be evaporated and this cannot be safely effected at a steam-heat. It has therefore to be done either at a gentle heat in the air, or in a vacuum over sulphuric acid. When the solution has been somewhat concentrated, say to a weight of 300 grams, it is cooled in ice and after some hours strained, still in the refrigerator, from a transparent magma of the crystals which have separated of sodium sulphate. Should the oximidosulphonate be wanted for the preparation of oxyamidosulphonate or, through this, of hyponitrite (*This Journal*, **3**, 211), the solution at this stage is serviceable without further preparation.

The solution, deprived of much of its sulphate by cooling, soon yields when restored to the vacuum-evaporator much of the sodium oximidosulphonate. 90 or 100 grams of this having crystallised out, its mother-liquor may be deprived of more sulphate by cooling and then yields a further crop of oximide crystals, nearly pure, by evaporation.

Even as first obtained, disodium oximidosulphonate is nearly pure, being an anhydrous salt in hard and dense small thick prisms deposited as a thick crust on the bottom of the crystallising pan. It may be recrystallised from its solution, made with a little hot water rendered slightly alkaline by ammonia, by evaporation.

Titration of some of the original liquor after hydrolysis of the salt into hydroxylamine, shows the yield to be 90 per cent., more or less, of the quantity calculated from the nitrite, but the crystals obtained do not amount to much more than 70 per cent., because the magma of sulphate retains much of the solution, which is very concentrated.

The theory of the formation of the oximidosulphonates is contained in the theory of the reaction between nitrites and sulphites, and this we hope to discuss in a future paper. It will be enough to point out here that one molecule of nitrite, one of hydroxide, and two of sulphur dioxide are by calculation convertible into oximidosulphonate and nothing else :—

$$NaNO_2+NaOH+2SO_2=HON(SO_3Na)_2.$$

It will therefore be seen that, with these proportions, were sulphite used instead of hydroxide or carbonate to begin with, the use of sulphur dioxide could still not be dispensed with. Cooling during the preparation of the solution guards against premature hydrolysis and lessens the production of nitrile. The quantity of water is limited because it has to be evaporated afterwards in the cold. Much less than the quantity prescribed will not be enough because then so much acid-carbonate or normal sulphite, as the case may be, may separate out in the middle of the process as to thicken the solution so that it cannot be sufficiently rapidly agitated with the sulphur dioxide to prevent the injurious action of local excess of the latter.

It is generally more convenient to work with sodium carbonate than with the hydroxide ; and on a large scale especially or on a moderately large scale, much more rapid working is possible with the carbonate than with the hydroxide, because of the much greater heat to be dealt with when the latter is used.

Preparation of the neutral potassium oximidosulphonate by using sulphur dioxide.—The process just described for getting sodium oximidosulphonate, but modified as to temperature, is eminently successful, and even simpler than when used for that salt, when employed for getting potassium oximidosulphonate from potassium nitrite and either carbonate or hydroxide. Other processes, already published, cannot approach it in certainty and in purity of the salt yielded. Over the process described in this paper (p. 19), in which are mixed somewhat more than three molecules of potassium metasulphite with two of nitrite, it has the same advantage, although in a less degree, and in addition that of not requiring voluminous solutions to be worked with. For it is still more certain than that process, and gives a yield in crystals of nearly 97 per cent. of the calculated quantity of the salt when carbonate has been used, and nearly 95 per cent. when hydroxide has been used, and with not enough nitrile with it to be visible, even on recrystallising. It is the small solubility of the potassium salt which makes its preparation simpler than that of the sodium salt, and also which, by throwing it out of solution removes most of it from the influence of the sulphite and sulphurous acid, and thus lessens the formation of nitrile. Our success by this method has been so much greater than that reached by either Claus or Raschig mainly because we have taken the nitrite and the hydroxide in the right proportion, besides guarding against local excess of sulphur dioxide, and being careful to preserve a low temperature.

Potassium nitrite, assayed for real salt, and either powdered potassium acid-carbonate or concentrated solution of potassium hydroxide in equal molecular proportions are put, with a weight of water about eight times that of the real nitrite, in a roomy flask kept at 0°, or even better at 2° or so below zero, by means of a brine bath with ice floating in it. To preserve this temperature during the passage of the sulphur dioxide the flask must be kept in active motion, with a thermometer in it for observation. By a wide inlet tube terminating high above the surface of the solution, in order to guard against its being choked, the sulphur dioxide is rapidly passed in until the carbonate has all dissolved and effervescence has almost ceased, or until the hydroxide, if that has been used, is nearly neutralised, and then passed slowly until the solution has become neutral to lacmoïd paper. The oximidosulphonate separates during the latter part of the process as a crystalline powder. The mother-liquor retains a little of it and contains, besides, some nitrile along with small quantities of both nitrite and sulphite. The precipitated oximidosulphonate can be dissolved in hot water containing for safety a little ammonia, and from the solution be got in good and characteristic crystals of great purity and comparative stability. The limit to the quantity of water to be used is given by the condition that there must be enough not to be thickened by the separation of the insoluble oximidosulphonate. When passing the sulphur dioxide into the flask closed with a cork holding inlet and outlet tubes and the thermometer, and with the inlet tube ending seven or eight centimeters above the surface of the solution, and even when the alkali is used as carbonate so that carbon dioxide is freely escaping, it is remarkable to observe the almost perfect absorption of the sulphur dioxide by the well-agitated solution.

Preparation of alkaline oximidosulphonates from the neutral salts.

Alkaline sodium oximidosulphonates.—The alkaline sodium oximidosulphonate, $Na_3NS_2O_7$, corresponding to Raschig's *basic potassium sulphazotate*, can be got by dissolving the neutral salt in water, adding just the calculated quantity of sodium hydroxide, and evaporating to the crystallising point in a vacuum desiccator. The possibility of preparing the salt in this way is of theoretical importance, but the salt, being less soluble in presence of sodium hydroxide, can also be prepared at once as a crystalline precipitate by adding the sodium hydroxide in excess to a concentrated solution of neutral sodium oximidosulphonate. The crystals are drained on a tile and recrystallised once or more by dissolving and evaporating.

A less alkaline sodium salt, $Na_8H(NS_2O_7)_3$, is obtained when a solution of the neutral oximidosulphonate is evaporated with somewhat less sodium hydroxide than is needed to form the above salt, such as half or more of that quantity. It can be purified by recrystallisation from water. It does not correspond in composition to Fremy's *basic sulphazotate* of potassium, being more alkaline than that salt.

Alkaline potassium oximidosulphonates.—The alkaline potassium salt, $K_3NS_2O_7$, discovered by Raschig, was obtained by him by dissolving the neutral salt in hot alkalised water, cooling rapidly, adding to the supersaturated solution cold concentrated potassium-hydroxide solution until it caused a troubling, and finally leaving the mixture to deposit the new salt in crystals. He also prepared it by adding an excess of very strong potassium-hydroxide solution to Fremy's basic salt already dissolved in a little warm water, and precipitating by alcohol.

Not only is excess of alkali useful here, as when preparing the sodium salt, by diminishing the solubility of the salt in its aqueous mother-liquor, it is also necessary, which is not the case with the sodium salt, to preserve the salt from decomposition by water. But when alcohol is to be used as the precipitating agent, the excess of alkali used by Raschig is uncalled for, equally as in the case of the sodium salt, and only the calculated quantity of potassium hydroxide having been added, a sufficiency of alcohol precipitates the salt. Indeed the best way to purify the salt from adhering alkali is to dissolve it in water and precipitate by alcohol, repeating the process once or twice.

The less alkaline potassium salt, $K_5H(NS_2O_7)_2$,—Fremy found that the neutral salt in the solid state combines at once with potassium hydroxide when treated with an excess of it in solution, and that the product dissolved up in hot water deposits his *basic sulphazotate* in crystals on cooling. We have fully confirmed Fremy's experience although from the fact of both salts being very sparingly soluble, the change of the powdered neutral salt into the alkaline one is not very apparent to the eye. Yet the potassium hydroxide is withdrawn by the powdered salt rapidly from the solution, which consequently loses all its causticity to the tongue. When used concentrated the alkali causes, as Fremy noted, a heating up, while when it is dilute it causes, we find, a fall of temperature amounting to about three degrees, due no doubt not to dissolution of salt so much as to liquefaction of three-fourths of the water of crystallisation of the neutral salt transformed.

Claus denied altogether that the neutral salt could be converted into the alkaline salt, and Raschig found it necessary for success to modify Fremy's process. The latter uses twice the calculated quantity of potassium hydroxide and in concentrated solution, heats to boiling, and crystallises the salt by cooling. The salt is purified by recrystallisation from water. Weak alkaline solutions of the neutral salt did indeed yield him crystals of the alkaline salt, but in order to do so had to be left to stand for some weeks. According to our experience, however, any excess of alkali is unnecessary and best avoided, as then the alkaline salt is at once obtained pure. Neither need the solution of the alkali be concentrated ; nor the mixture be heated to boiling ; nor time be given, more than is usual for crystallising out salts. When crystallisation happens to be slow in setting in, a particle of the solid salt, previously obtained, at once determines it when dropped into the solution.

Alkaline potassium sodium oximidosulphonates.—There is some difficulty in preparing potassium-sodium salts having a basicity as great as that of the more alkaline sodium or potassium salt, but several less alkaline can be obtained by mixing in solution the neutral potassium salt with sodium hydroxide, or the neutral sodium salt with potassium hydroxide, and either evaporating or adding alcohol.

Alkaline barium, strontium, and lead salts.—Addition of barium hydroxide or of oxy-lead acetate to a solution of neutral potassium, sodium, or ammonium oximidosulphonate causes precipitation of an alkaline or ' basic ' salt. Strontium hydroxide gives a precipitate of alkaline salt with potassium oximidosulphonate almost immediately ; it gives no precipitate with sodium or ammonium oximidosulphonate, but causes an alkaline salt to crystallise out in a few hours.

Decomposition of chlorides and nitrates by the neutral oximidosulphonates.—The neutral potassium salt in solution with potassium chloride, potassium nitrate, or sodium chloride, yields when treated with strong ammonia-water, alkaline oximidosulphonates either at once or after evaporation, ammonium chloride or nitrate being formed.

Decomposition of carbonates and of acetates by the neutral oximidosulphonates.—When a warm solution of sodium or potassium carbonate is saturated with the neutral potassium oximidosulphonate, the less alkaline potassium-salt or an alkaline potassium-sodium salt crystallises out on cooling. Neutral sodium or potassium oximidosulphonate evaporated with either sodium or potassium acetate gives off acetic-acid vapours and yields a highly alkaline solution (of alkaline oximidosulphonate).

Reconversion of alkaline into neutral and less alkaline oximidosulphonates.

The conversion of the more alkaline back into the alkaline, and of these again into the neutral oximidosulphonates, described in this section, and the conversion of neutral into alkaline oximidosulphonates, described in the preceding section, demand particular attention as being facts opposed to the view maintained by Claus and by Raschig that Fremy's sulphazotates include the salts of two distinct acids.

Solutions of the more alkaline and the neutral sodium oximidosulphonates evaporated together, best in a vacuum desiccator, are converted into the less alkaline salt in crystals. Two equivalents of the former combine with one of the latter, and this happens even when only one equivalent of the former salt is taken, excess of the latter then remaining in the mother-liquor. We find also that, when a concentrated solution of the more alkaline potassium salt is mixed with a cold supersaturated solution of the neutral potassium salt in equivalent quantity, crystallisation of the less alkaline salt soon sets in, or else can be at once determined by adding a crystal of this salt.

Conversely, in a manner, as Fremy found, the less alkaline salt is resolved, when treated with the solution of a lead or a barium salt, into the neutral salt and the more alkaline salt, the latter becoming by the reaction an insoluble salt of lead or barium with potassium. Indeed, this conversion is the basis of one of Fremy's methods of getting the neutral potassium salt. Fremy's observations were emphatically discredited by Claus and ignored by Raschig.

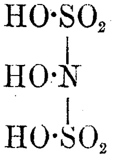
Weak acids—including sulphurous acid (*cf.* Fremy)—and even strong acids diluted and cautiously used, convert the alkaline salts into the neutral, when added not in excess so as to hydrolyse the oximidosulphonate. Claus strongly denied this to be the case, but Fremy was right. Metasulphites also, added not in excess, remove alkali from the alkaline salts, they themselves becoming thereby normal sulphites, as shown by the mixed solutions being neutral to rosolic acid.

Several metallic salts such as those of zinc and manganese behave like acids with the alkaline salts, converting them into the neutral salts, and depositing their own metal as hydroxide, as was observed by Fremy. Water alone when present in large quantity suffices to convert the more alkaline potassium salt into the less alkaline salt along with potassium hydroxide (*cf.* Raschig), but has little if any action upon the sodium salt.

Constitution.—Unity of oximidosulphonates and sulphazotates.

The constitution of the oximidosulphonates as sulphonic derivatives of hydroxylamine follows from the fact of their formation by the union of nitrite with sulphite, and from that of their hydrolysing in stages into hydroxylamine and sulphate. From the account we have given—and Fremy before us—of the conversion of the neutral into the alkaline, and of the alkaline into the neutral salts, it might also be accepted without hesitation that they are all the salts of one acid, were it not for the dissent of Claus and of Raschig from this conclusion.

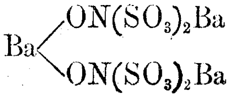
All the compounds described in this paper seem to us to be as clearly salts of one acid as are the acid, neutral, and alkaline orthophosphates all salts of one phosphoric acid. This acid, Fremy's sulphazotic acid, is oximidosulphonic acid, a tribasic acid with the constitutional formula :—



$$\begin{array}{c} HO\cdot SO_2 \\ | \\ HO\cdot N \\ | \\ HO\cdot SO_2 \end{array}$$

and unknown as the wholly hydrogen salt. Of this acid the salts with neutral or slightly acid reaction are monohydrogen salts, and those with three monad atoms of metal (or their equivalent) which we have hitherto designated *the more alkaline* salts are normal salts. For example :—

$HON(SO_3Na)_2$; $NaON(SO_3Na)_2$;



The less alkaline salts, called in the case of potassium, *basic sulphazotate* by Fremy and *sulphazotate* by Claus and by Raschig, are double salts of the normal and the acid or hydrogen salts, thus :—

$$HON(SO_3K)_2, KON(SO_3K)_2 \text{ and } HON(SO_3Na)_2, 2\,NaON(SO_3Na)_2,$$

pentapotassium bi-oximidosulphonate and *octasodium ter-oximidosulphonate.*

Nothing is wanting in the evidence to the truth of the views here set down. Any acid serves to replace in the normal salts the third atom of metal by hydrogen; many salts, such as zinc sulphate, do the same (p. 33) ; potassium or sodium hydroxide directly reacts with the hydrogen salts to replace some or all of the hydrogen by metal, and just as readily as it does with phosphoric acid, which, as is well known, does not exchange all its hydrogen for metal unless the alkali is used in good excess.

That the pentapotassium and octasodium compounds are double salts is a conclusion in accordance with all that is known of them. They are formed by the simple union of the hydrogen salt with the normal salt in solution, even when the quantities of these salts deviate to a not inconsiderable extent from their proportions in the compound salts, and they have an action on litmus, phenolphthaleïn, etc., the same as that of the normal salts alone. In reaction they decompose into their component salts, one only being active. Fremy observed that lead and barium salts added to a solution of the pentapotassium salt gave precipitates more basic than it and left in solution the neutral potassium salt ; but as he did not know of the existence of the normal potassium salt, and got complex basic precipitates, he could not represent the change quite as we do. Even now it still remains open to say with him that a basic salt precipitating, the acid of the precipitant converts another portion of the alkaline potassium salt into the neutral one, though to do so is to pay no consideration to the fact that normal salts are known and that the barium salt is one of them and the lead salt another, though in this the lead is half as hydroxide. It seemed of interest to examine the precipitation by barium chloride quantitatively. Adding this salt in moderate excess to a solution of the pentapotassium salt, the proportion of oximidosulphonic radical precipitated was found to be eight-nineteenths of the whole, a result which, after allowing for the solubility of barium oximidosulphonate, may be accepted as proof that the pentapotassium salt had acted as tripotassium salt united with indifferent dipotassium salt.

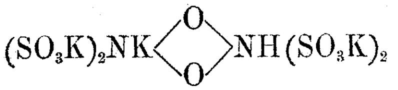
One thing more is to be pointed out in support of the double-salt character of the pentapotassium oximidosulphonate. Although this salt so readily and frequently crystallises from solution as to have become the best known of the three potassium salts, matters are quite otherwise with the sodium salts among which the pentasodium salt cannot even be prepared at all; the salt intermediate to the normal sodium and the disodium salts which can be formed is troublesome to get; and the normal salt itself is that which readily crystallises out from a sufficiently alkaline solution.

There is a strikingly characteristic test for these salts in common, from which it may be assumed that they have a common constitution. Both neutral and alkaline oximidosulphonates, and no other salts, yield in solution, at once and in the cold, an intensely coloured salt when gently oxidised in the absence of acids, the reaction being one of the most remarkable in the domain of inorganic chemistry (p. 46). This reaction was described by Fremy and his accuracy fully confirmed by Raschig.

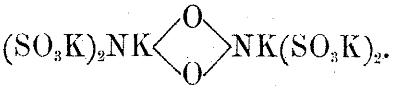
Failing entirely to convert Fremy's two potassium sulphazotates into each other, or believing that he had failed, Claus held them to be salts of distinct acids and gave them the distinctive formulæ—

$NHO(SO_3K)_2$ and $NH(SO_3K)_3{\cdot}NO(OK)(SO_3K)$—with the nitrogen quinquevalent. He believed that he had evidence of the latter salt being always formed from the nitrile, $N(SO_3K)_3$, which for him was trisulphammonate, $NH_2(SO_3K)_3$. Claus's observations and conclusions were examined at length by Raschig and satisfactorily refuted by him: they need not, therefore, be discussed by us.

Having rejected Claus's views, Raschig gave the hydroxylamine constitution to the neutral salts, but proposed another constitution for the two alkaline salts, in which like Claus he made the nitrogen quinquevalent:



and



The character of this constitution need not be noticed here: we shall probably return to it in our paper on the *sulphazilates.*

One argument given by Raschig for regarding as distinct the acids of the neutral and alkaline salts was, that although acids at once convert the latter salts into the former, alkalis effect the opposite change only with difficulty. Weak alkali, he found, requires weeks and to be in excess in order to effect the conversion; while a concentrated solution of alkali must be, in order to act quickly, boiling hot and also in excess. Our experience, recorded on page 31, lends no support to this finding. The delay he observed in the appearance of crystals of the salt, a fact to which he attached weight, must have been due to the salt remaining in supersaturated solution, although he himself dismissed this explanation of the matter as inapplicable, averring that this salt when obtained does not show the phenomenon of supersaturation, without however testing the matter by adding a bit of the salt to excite crystallisation. The salt does not indeed supersaturate its solutions to the degree shown by the neutral potassium salt, but nevertheless its hot strong solution in simple water can be rapidly cooled and then kept for an hour or more without crystallising, and nothing can be objected to allowing that it may show still greater supersaturation in presence of the other salts of its mother-liquor. Mixtures made to prepare it, yield it at once if cold when a crystal of it is dropped in or when alcohol is added, free alkali remaining in solution in the latter case, only when in excess of that required to form the normal salt, and this salt occurring in the alcoholic precipitate when the alkali is in excess of that necessary to the composition of the pentapotassium salt. But apart entirely from this matter of supersaturation, there is in proof that cold dilute alkali converts the neutral salt at once into the alkaline salt, Fremy's experiment, repeated by us, of acting upon the solid neutral salt with potassium hydroxide in aqueous solution (p. 30). The neutral sodium salt also passes readily and at once into the normal salt on adding sodium hydroxide to it.

Raschig gave as a chemical property distinguishing between the neutral and alkaline salts, the activity of alkali sulphite upon the former and inactivity upon the latter. We have not succeeded ourselves in finding anything in Claus's writings upon this subject, but Raschig adduced Claus in evidence of his statement. Fremy's writings, however, are sufficient to show that the above distinction, so far as it holds good, serves only to mark the alkalinity of the alkaline salt, for he points out that sulphurous acid first converts the basic sulphazotate to the neutral sulphazotate and then acts upon this salt. To this we may add that metasulphite and alkaline oximidosulphonate change together into normal sulphite and neutral oximidosulphonate, and that when enough metasulphite is added all oximidosulphonate is quickly destroyed.

There yet remains for consideration one other ground taken by

Raschig for separating the alkaline sulphazotates from the neutral salts. According to him, there is a salt isomeric with Fremy's basic sulphazotate which, unlike this, cannot be recrystallised from water, its alkaline solution depositing neutral oximidosulphonate. It, therefore, rather than Fremy's basic sulphazotate, must be held to be half-basic oximidosulphonate. The Fremy-Claus process for preparing neutral oximidosulphonate had yielded him the new salt but this was only once, and many repetitions of the process failed to reproduce it.

The difficulties in the way of accepting the existence of this salt as proved are very great. As just stated it could not be got again by the process which had apparently yielded it. Moreover it cannot be got by treating the neutral salt with potassium hydroxide, and it is hard to see why, if it is a basic derivative of that salt decomposable by water. Neutral oximidosulphonate recrystallised from water holding potassium hydroxide is strongly alkaline, so that Claus found the percentage of potassium to become some units higher than in the pure salt, and such a preparation behaves with water like Raschig's salt. But, according to Fremy and us, there is here only the production of some basic sulphazotate, and recrystallisation from water separates the two salts. Now, the process which gave Raschig his salt may, according to Claus, give not only the neutral salt but also some basic salt, and therefore a combined product behaving with water like Raschig's preparation.

But if we accept the results of the analysis of the salt, it could not have been other than a new salt, for Fremy's basic sulphazotate does not decompose with water into the neutral salt. We are strongly of opinion, and venture here to suggest that some mistake such as may happen to any one at times, crept into Raschig's work or the record of his work. He made but one analysis, and in that determined only the potassium and the sulphur. Of these two the sulphur content happens to be a factor of no account in the present case, for the percentage of sulphur is nearly the same in the neutral and the basic sulphazotate (or its isomer), namely, 20·97 and 21·53, and Raschig's preparation could not from the circumstances claim any high degree of purity. There is, however, a wide degree of difference between the percentage of potassium in the neutral and that in the basic salt, and that got by Raschig agrees well with that for the basic sulphazotate with its one molecule of water of crystallisation. But here Raschig himself comes, as it were, to our assistance, and this emboldens us to ask for some distrust of his potassium number, for he actually discusses (though only to reject on experimental grounds) the possibility of his salt being Fremy's sulphazate, which does not differ ' so very much ' from it, he says, in the amount of sulphur,—although that difference is really $3^1/_2$ per cent. Now, let such a lowering as this be made in the potassium percentage and the sulphur be allowed to stand, and we should have a sulphazotate mixture or compound resolving itself, as Raschig's preparation did when dissolved in water, into the two salts. In concluding this criticism we may add that Raschig ends by affixing a note of interrogation to the formula of his salt.

Reversion of oximidosulphonates to nitrite and sulphite.

Sodium or potassium oximidosulphonate digested in the cold for some hours with highly concentrated solution of sodium or potassium hydroxide, or boiled with it for a few minutes, is largely converted into nitrite and sulphite. Some of the latter salt crystallises out, and the solution evolves sulphur dioxide and oxides of nitrogen when acidified, or when neutralised and mixed with barium chloride gives a precipitate of barium sulphite, leaving nitrite in plenty in solution, easy then to detect. The following equation expresses this change :—

$$KON(SO_3K)_2+2KOH=H_2O+KNO_2+2K_2SO_3\ ;$$

but the reversion is attended with some other changes resulting in the escape of nitrous oxide and perhaps nitrogen, a consideration of which will be found following the paragraphs on hydrolysis (p. 42).

The normal salts in solution, or as solids not quite free from moisture, soon suffer some reversion in the cold, and very much more when the solutions are boiled, without any alkali being added:—

$$KON(SO_3K)_2=KNO_2+K_2S_2O_5$$

The five-sixths normal potassium salt, although when well prepared and preserved in a dry atmosphere it can be kept for months without suffering noticeable change, is when damp unstable, as found by Claus and Raschig. But even the best preparations of it prove at last unstable, and we have found that this is due to the reversion which slowly goes on in it:—

$$K_5H(NS_2O_7)_2=K_2HNS_2O_7+KNO_2+K_2S_2O_5$$

Such a mixture of salts must be very unstable, liable to hydrolysis and other changes, sufficient to account for that entire break-up of the salt which finally happens. Even before the change has proceeded far enough to affect the appearance of the crystals, the reversion can be detected by the presence of sulphite. For this detection direct acidification of the salt is hardly effective, because of secondary reactions which then consume the sulphurous acid. But by dissolving the salt, thus slightly decomposed, in water, adding barium chloride, and acidifying the washed precipitate, the sulphite can be readily found.

The disodium and dipotassium salts should, as neutral or nearly neutral salts, be liable to neither reversion nor hydrolysis, but their equilibrium is so unstable that the fact is that they are especially prone to rapid change. It is probable that they do really suffer no reversion, but in practice, in consequence doubtless of the traces of alkaline salt purposely left in them as a guard against rapid hydrolysis, they do when kept dry develope a little sulphite before they hydrolyse. The disodium salt, which is an anhydrous salt, may however be kept for years in a desiccator without suffering sensible reversion. In comparison with the others, the five-sixths normal potassium salt and the disodium salt are the salts of their respective metals best fitted to keep in stock for any considerable time.

The dry lead salt reverts when heated. This salt is a basic or hydroxy-salt, and when moderately heated is decomposed, thus :—

$$(HOPb)_3NS_2O_7 = HOPbNO_2 + 2PbSO_3 + H_2O$$

The residue if further heated evolves red fumes, and if moistened with sulphuric or hydrochloric acid evolves much sulphur dioxide.

Other chemical properties of oximidosulphonates.

Hydrolysis.—The hydrolytic decomposition of oximidosulphonates has been repeatedly referred to in this paper, and is besides a fact long known. Its almost inevitable occurrence in every alkali oximidosulphonate is all that needs further notice. When by circumstances or by intention the salt is rendered acid, hydrolysis always quickly ensues. An alkaline salt when there is any water available, always becomes acid in time by suffering reversion, and thus its hydrolysis is brought about.

In dilute solutions of oximidosulphonates acidified, hydrolysis proceeds without complication, but in strong solutions, and when the change is carried through, by heating, to hydroxylamine sulphate, some gas is produced,—nitrous oxide and nitrogen. In hydrolysing for analytical purposes, this is manifested by pressure in the sealed tube, and by a deficiency in the quantity of hydroxylamine (*cf.* Raschig).

When moistened dipotassium oximidosulphonate hydrolyses spontaneously, it also gives out at the same time much nitrous oxide and a little nitrogen, while strong hot solutions of it or of the disodium salt effervesce a little when acidified.

Dipotassium salt which has been preserved as far as possible in a desiccator, also effervesces when dissolved in water, even in presence of an alkali. In these changes a little ammonia is also generated.

It thus appears that oximidosulphonates decompose in several ways combined; by reversion, by hydrolysis, and by secondary reactions with the sulphurous acid generated by the other changes. As products we therefore get in the first line, nitrite, sulphite, oxyamidosulphonate, and sulphate. From the sulphite and oxyamidosulphonate we may get imidosulphonate hydrolysing to amidosulphonate, and from the sulphite and oximidosulphonate, nitrilosulphonate. By the hydrolysis of the oxyamidosulphonate there will be got hydroxylamine, and by its reversion, hyponitrite. From the hydroxylamine or from the amidosulphonate (slowly) may come ammonia, and from the former in alkaline solution also nitrous oxide and nitrogen. Nitrous oxide may also come from hyponitrite, and from hydroxylamine and nitrous acid, and nitrogen from ammonia and nitrous acid. But with all these possibilities before us, there are points which remain obscure, particularly that in the acid-decomposition of oximidosulphonates nitrous oxide and nitrogen should be evolved.

Behaviour when heated.—The dipotassium salt hydrolyses with its water of crystallisation quite suddenly when heated to 90° in a limited space, but by very gradual heating in a roomy air-bath it can be rendered anhydrous and raised to 100° and a little above without change (Claus). The disodium salt, which is anhydrous, can be safely heated to the same extent. In a current of dried air both salts can be heated much above

100° without being changed. The alkaline salts, though they contain water, may be heated also without change to 100° or a little above.

About 105° for the two-thirds normal salts and 110° for the alkaline salts, oximidosulphonates slowly take moisture from the air, increase consequently in weight, and become hydrolysed and acid. In this behaviour they are like imidosulphonates (*This Journ.*, **6**, 64). Claus observed that the dipotassium salt gained thus in weight, but set this down to absorption of oxygen. But any oxidation would be attended with a loss of nitrogen or oxides of nitrogen much more in weight than the oxygen absorbed. Besides, we find that, heated for hours at 120° in a current of well-dried air, oximidosulphonates, even the two-thirds normal potassium salt, gain nothing in weight.

The effect of higher temperatures was investigated by Claus, who found that the anhydrous dipotassium salt gives off some acid-reacting vapour not sulphur dioxide, that on further heating a little ammonium sulphate sublimes (!), and that the residue then consists apparently of potassium pyrosulphate. His experience on heating the five-sixths normal potassium salt was, that above 200° the crystals swell up and spring asunder, give first nitric oxide and then ammonium sulphate, and leave a residue which does not fuse and is normal potassium sulphate. Fremy, Claus, and Raschig all state that this salt decomposes suddenly at about 200° (150° Raschig) with development of red vapours.

We have experimented more particularly with the sodium oximidosulphonates, the disodium salt being better fitted than the dipotassium salt for testing the effects of dry heat upon oximidosulphonates because it is anhydrous. With the object of collecting the resulting gases the heating has been conducted in a vacuum as well as in open vessels.

The dried normal sodium salt remains unchanged until the temperature has risen to 182–3° when it suddenly decomposes into a loose unfused residue, vapours depositing a very small sublimate, and gases. The residue is neutral or slightly alkaline and consists of sodium sulphate with a very little thiosulphate. The very small sublimate consists of sulphur and ammoniacal salt which when acidified yields a solution milky from sulphur and smelling faintly of sulphur dioxide. The gases are sulphur dioxide and nitrogen in nearly equal volumes.

Neglecting the very small quantities of sulphur, thiosulphate, and ammonia, all due to water retained by the salt, the decomposition may be written:—

$$2Na_3NS_2O_7 = 3Na_2SO_4 + SO_2 + N_2.$$

The anhydrous disodium salt begins to give off gas in a vacuum, but exceedingly slowly, at about 140°, and continues to do so nearly as slowly while the temperature is rising to about 170°, or while it is maintained steadily at any intermediate point. When the temperature is allowed to rise continuously though slowly the full decomposition of the salt occurs suddenly at 171°, whilst when it is kept steady for an hour or more at about 165° and then slightly raised, full decomposition occurs suddenly at 167–8°. At the moment of active decomposition the salt fuses and effervesces and, like the trisodium salt, yields a small sublimate as well as gases. The residue is exceedingly acid and consists of sodium acid-sulphate with a not inconsiderable quantity of ammonium acid-sulphate or more probably the corresponding pyrosulphates. The sublimate is a compound of ammonia and sulphur dioxide while the gases consist of nitrogen and sulphur dioxide, the former in somewhat greater volume than the latter. Nitrous oxide could not be detected by us; but in one experiment the sulphur dioxide constituted more than half the total gas, a result only to be explained as due to some undetected error or to the presence of a little nitrous oxide along with the nitrogen. The nitrogen obtained was about four-fifths of the total nitrogen of the salt, the rest remaining in the residue as ammonia. So far as was ascertained—and observation is difficult because of the explosive character of the salt—the first portions of gas are richer in sulphur dioxide than the last. If this be really so, it points to the not improbable intermediate formation of some imidosulphonate.

From the facts observed, the decomposition of the disodium salt seems to vary between that expressed by—

$$2Na_2HNS_2O_7 = 2NaHSO_4 + Na_2SO_4 + SO_2 + N_2$$

and that expressed by—

$$8Na_2HNS_2O_7 = 3Na_2SO_4 + 5Na_2S_2O_7 + (NH_4)_2S_2O_7 + 3N_2 + SO_2.$$

It will be seen that our observations do not agree with those made by Claus as to the nature of the products of the decomposition of oximidosulphonates by heat. Fremy, Claus, and Raschig all state that the five-sixths normal potassium salt gives red fumes when heated, and this also we cannot confirm; whether in crucible or in tube, heated slowly or quickly, it has never given us such fumes. Only where reversion to nitrite and sulphite has taken place, as with lead oximidosulphonate already noticed, does heat generate red fumes.

Oxidisability.—Characteristic of the oximidosulphonates are, firstly, that they do not reduce copper salts in presence of alkali, unless they have been previously hydrolysed with acid; secondly, that they yield by gentle oxidation Fremy's *sulphazilates*, unstable salts, blue-violet in solution, yellow and crystalline in the solid state. Traces of almost any oxidising agent capable of acting in alkaline solution effect this change in the alkaline salts, but oxidising agents of a basic character act also on the neutral salts. Silver oxide and lead peroxide are the best reagents for detecting any oximidosulphonate. These oxides were used by Fremy. In hot acid solution oximidosulphonates are converted into sulphates and oxides of nitrogen by oxidising agents, such as nitric acid, bromine, and potassium chlorate, but the decomposition is seldom so complete as to be available for determining sulphur quantitatively.

Action of strong sulphuric acid.—That strong sulphuric acid disengages nitric oxide, as stated by both Fremy and Claus, we cannot admit. Heated with this acid, a sodium or potassium salt dissolves and evolves no gas until sulphuric-acid vapours are freely escaping, when nitrous oxide and sulphur dioxide are slowly generated. Indeed, addition of sulphuric acid should be made before igniting oximidosulphonates for analytical purposes, in order to avoid loss through explosive decomposition.

Behaviour with other salts in solution.—Disodium, dipotassium, or diammonium oximidosulphonate does not precipitate other salts and appears often not even to react with them, since on evaporation the salts mixed together crystallise out unchanged. This interesting fact was observed by Fremy in the case of the dipotassium salt mixed with those of zinc, manganese, copper, and silver. Claus denied its truth. We have fully verified it in the case of the disodium salt and copper sulphate. These salts in about equivalent quantities were dissolved in water and the solution made slightly turbid with copper hydroxide by adding a minute quantity of sodium hydroxide, in order to guard against hydrolysis supervening. By spontaneous evaporation copper sulphate first crystallised out and then the sodium oximidosulphonate, that is, in the order of their solubilities. This behaviour of the alkali oximidosulphonates serves to show that as sulphonates they have the stability of sulphates themselves.

A normal alkali oximidosulphonate reacts generally as alkali hydroxide towards salts the hydroxides of whose bases are insoluble ;

disodium, potassium, or ammonium oximidosulphonate remaining in solution. Silver oxide thus formed acts slowly as an oxidising agent. Triammonium oximidosulphonate added in excess to copper sulphate gives a chromium-green solution, which is turned blue by ammonia and which with excess of copper sulphate behaves as usual, yielding a precipitate of copper hydroxide and leaving diammonium oximidosulphonate in solution.

However, both the two-thirds normal and the normal salts of the alkalis enter into some reactions of complete double decomposition. Thus, either a two-thirds normal or a normal oximidosulphonate precipitates with hydroxy-lead acetate in excess or with barium hydroxide ; a normal salt precipitates also with sufficient normal lead acetate or with barium chloride ; but to secure precipitation of a lead salt the solutions must be dilute. The barium precipitates, too, are very slightly soluble in solutions of alkali oximidosulphonates. Calcium compounds yield no precipitates, but its hydroxide forms salts by decomposing the ammonium oximidosulphonates. Strontium compounds give with potassium oximidosulphonates clear solutions for a moment which then become filled suddenly with a voluminous silky precipitate. Fremy could get no precipitate with strontium salts, nor Claus either, strange to say. With sodium or ammonium oximidosulphonates, strontium salts do not precipitate, but in a few hours the solution deposits silky crystals in large hemispherical groups on the sides of the vessel.

The precipitates of barium, strontium, and lead salts are soluble in acids and in ammonium salts including ammonium oximidosulphonates. The lead precipitates are also soluble in sodium or potassium hydroxide.

Barium sulphate is distinctly soluble to a small extent in solutions of the normal alkali oximidosulphonates. Thus, barium chloride may be added in very small quantity to a solution, not too dilute, of a normal alkali oximidosulphonate containing sulphate without occasioning any permanent precipitate even on standing. But when the alkalinity of the solution is about neutralised with hydrochloric acid, the solution becomes turbid from the separation of barium sulphate.

The purified barium or lead oximidosulphonates can be decomposed by sulphates and very completely by carbonates, and thus be used to furnish other oximidosulphonates. The ammonium salts which can be formed in this way serve in turn for the preparation of salts of metals which do not unite with ammonia by evaporating their solution with the oxide or hydroxide of the metal. However, the oximidosulphonates obtained in this way are the more unstable of these salts and we have not pursued their examination.

Oximidosulphonates combine readily with each other and with other salts, a fact which will be made fully evident in the brief descriptions which follow of the salts we have prepared.

Sodium oximidosulphonates.

Normal sodium salt, $Na_3NS_2O_7,3H_2O$.—This salt forms rhombic prisms often a centimetre in length. It is strongly alkaline, soluble in 1·3 parts of water at 20°, and tends to form supersaturated solutions. It is only partly precipitated by alcohol but without decomposition, and is less soluble in sodium-hydroxide solution than in water. Its analysis gave—

	Calc.	Found.
Sodium	22·05	21·94
Sulphur..................	20·45	20·38
Oximide residue	9·58	9·32
Water	17·28	17·86

This and other oximidosulphonates were decomposed for the estimation of hydroxylamine and sulphuric acid by hydrolysing in sealed tubes with dilute hydrochloric acid kept for some time at 100° and only then heated to 130°. Some of the attempts to estimate hydroxylamine were however defective for the reason already given (p. 42). The sodium was directly estimated by cautious ignition with sulphuric acid, the presence of which prevents explosive decomposition of the salt by heat.

Disodium salt, $Na_2HNS_2O_7$.—This salt is anhydrous and is soluble in somewhat more than its own weight of water at 14°. It just reddens litmus. Its crystals are usually small, dense, brilliant prisms, united into hard masses and firmly adhering to the glass. On analysis it has given :—

	Calc.	Found.	
Sodium..............	19·41	19·21	19·53
Sulphur	27·00	27·06	26·98

Eight-ninths normal sodium salt, $Na_2HNS_2O_7$, $2Na_3NS_2O_7$, $3H_2O$.—The solutions intermediate in composition to those of the trisodium and disodium salts which yield this when evaporated may be prepared by adding either sodium hydroxide or trisodium salt to a solution of disodium salt in approximately the calculated quantity. Twice, when the solutions were left in the desiccator to evaporate and were of the composition of the unknown five-sixths normal salt, good sized prisms and plates of some salt filled the solution which when the attempt to remove them was made, rapidly melted away very remarkably, to give place to a precipitate of the eight-ninths sodium salt. Possibly, they were crystals of the five-sixths salt. The eight-ninths salt, redissolved in water or in its diluted mother-liquor, gives on evaporation small nodules of the salt. Only under the microscope can this precipitate and these nodules be made out to be composed of prismatic crystals. The crystals are efflorescent. Like the other sodium salts this one is exceedingly soluble in water, requiring less than 1·5 parts of water at 14° to dissolve it, and can be repeatedly recrystallised unchanged. It tends greatly to form supersaturated solutions. We have made the following analyses of it prepared under different conditions :—

	Calc.	Found.			
		(a)	(b)	(c)	(d)
Sodium	22·77	22·51	22·64	22·63	22·77
Sulphur	23·73	23·76	24·04	23·73	23·49
Oximide residue......	11·13	11·14	—	11·13	—
Water	6·68	3·59	3·53	—	—
Alkalinity, sodium...	5·69	—	5·45	—	5·83

The alkalinity of the preparations was determined with decinormal acid and methyl-orange. The water was estimated by drying at 110°, and it will be noticed that half of it was retained at this temperature. Similar retention of water will be seen in the case of the five-sixths potassium salt, of one of the sodium-potassium salts, and in that of the barium salts, and is not due to the fixation of the water by hydrolysis. It is remarkable that there should be such a difference in this respect between this and the normal salt.

Preparation (*a*) was deposited by evaporation in the cold of a solution of two molecules of the disodium salt to one of sodium hydroxide ; preparation (*b*) was the same salt recrystallised from water and separated as a precipitate from the supersaturated solution by stirring ; (*c*) was obtained by evaporating the mother-liquor of (*b*) ; and (*d*) was prepared by evaporating a solution of the calculated quantities of the disodium and trisodium oximidosulphonates.

Potassium oximidosulphonates.

Normal potassium salt, $K_3NS_2O_7, H_2O$. Also $K_3NS_2O_7, 2H_2O$.—We have several times prepared and analysed this salt with results very nearly agreeing with those got by Raschig. But while he has given to the salt only one molecule of water to $K_6N_2S_4O_{14}$, we find that there is one molecule to $K_3NS_2O_7$. Neither he nor we happen to have succeeded in getting, the salt quite free from excess of alkali: we say 'happen,' because we are sure that we could prepare it so. Tabulating his and our analyses which show least excess of alkali with calculations for his formula and for ours—

A	*Raschig.*		*Divers and Haga.*	
	Calc.	Found.	Calc.	Found.
Potassium	37·09	36·67	36·06	36·29
Sulphur	20·25	19·33	19·67	19·42
Water	2·85	—	5·53	5·61

—we see that his analysis is less incompatible with our formula than with his, for which his sulphur is much, and inexplicably, too low, while agreeing with his other and all our determinations of sulphur. We estimated the water in our preparation, and it will be seen that potassium, sulphur, and water all agree well with our formula. Our analysis was made on a precipitate got by adding alcohol to a solution of dipotassium salt and potassium hydroxide in about the calculated proportions.

We now tabulate the other analyses by Raschig and by us along with a calculation for $K_3NS_2O_7,{}^1/_8KOH,{}^5/_8H_2O$ which matches Raschig's preparation:—

B		*Raschig.*	*Divers and Haga.*	
	Calc.		(*a*)	(*b*)
Potassium	37·53	37·55	37·48	37·37
Sulphur	19·66	19·56	19·23	19·54
Water............	4·15	—	3·86	—

Our (*a*) preparation was got by using excess of concentrated alkali, was drained on the tile, and then washed with alcohol ; (*b*) was got by recrystallising from water an unwashed salt like the last. This was the only time we succeeded in recrystallising the salt from water without adding fresh alkali. It will be seen that both Raschig's results and ours agree much better in composition with the formula of an impure salt than with that for a salt with half a molecule of water to one molecule of oximidosulphonate, (A) and from such results no deduction can be safely made as to the degree of hydration of the pure salt.

We once obtained the normal potassium salt crystallised with two molecules of water. The salt precipitated by adding excess of potassium hydroxide, and drained on the tile, was redissolved in water and precipitated by alcohol. In other trials in this way we got the salt with only one molecule of water as above. Our analysis included the estimation of the oximide radical as hydroxylamine :—

	Calc.	Found.
Potassium	34·17	34·10
Sulphur..................	18·64	18·81
Oximide residue	8·74	8·44

Dipotassium salt, $K_2HNS_2O_7,2H_2O$.—Besides the two excellent methods of preparing this salt from potassium nitrite it can also be obtained, sometimes conveniently, from the disodium salt by precipitating this with potassium chloride, and is then more certainly free from nitrilosulphonate. The yield in this way can be made as much as 80 per cent. of the equivalent of the quantity of disodium salt taken. Fremy's method of preparing it pure from the alkaline five-sixths potassium salt by precipitating this with zinc or lead or barium salt thus leaving the dipotassium salt in solution, and which did him good service, is now only of interest as establishing the two potassium salts as salts of one and the same acid.

The dipotassium salt forms detached hard crystals remarkable in shape, being like somewhat flattened, very acute octahedrons. The crystals belong to the oblique rhombic system (Raschig and Fock). The analyses of Claus and Raschig established the composition of this salt. Fremy's recorded results are improbable and insufficiently concordant ; but the identity of his *sulphazotate* with dipotassium oximidosulphonate is beyond doubt.

According to Claus, the dipotassium salt is practically insoluble in cold water, and is very difficultly soluble according to Raschig. Its crystals can indeed be washed without much loss, but the salt in fine powder proves to be far from insoluble. It dissolves to the extent of about one part in thirty of water. When quite free from alkaline salt, it is faintly acid to litmus. It readily forms supersaturated solutions, as observed by Raschig, and in the preparation of the salt the mother-liquors retain much more of it than could simple water. We find that of a saturated solution of sodium chloride about 4 cub. cent. are able to dissolve 1 gram of the dipotassium salt, but the solution quickly deposits a compound of the two salts. Other salts also increase its solubility. Potassium or sodium hydroxide or normal oximidosulphonate acts upon it and thus affects its solubility.

Five-sixths normal potassium salt, $K_2HNS_2O_7, K_3NS_2O_7, H_2O$.—There is really only one way of preparing this salt, namely, by dissolving up the dipotassium salt in hot solution of enough potassium hydroxide (or salts equivalent to it) and crystallising. The dipotassium salt should not be put into cold water or even potassium hydroxide, and then the vessel heated to dissolve it, unless the mixture is continuously stirred ; for undissolved salt lying on the hot bottom of the vessel is liable to hydrolyse. Observing this precaution, no simpler way could be conceived to prepare the salt, all difficulties being imaginary. The belief that the salt can be formed from the nitrite direct is unfounded in fact, the dipotassium salt always preceding it and then only yielding it by alkaline treatment.

The five-sixths potassium salt forms rhombic plates, crystallising in masses on the walls of the vessel. It is only sparingly soluble in water. It was analysed by Fremy and by Claus with results identical as to the sulphur and not greatly differing from each other as to the potassium. Raschig got results for potassium exactly intermediate to theirs, but for sulphur one per cent. less than they got; and he rightly gave to the composition of the salt a molecule of water, although Claus had emphatically stated it to be anhydrous, having found that it can be heated to 120° without any change or loss of weight. Raschig, however, so far from establishing the presence of this molecule of crystallisation-water, wrote of the salt that it 'remains wholly unchanged at 120°,' a statement almost the same as that which Claus had made in proof that it contained no water. The facts, we find, are that it does lose in weight when heated, in fine powder, to 120°, and therefore contains water, but, as is usual in our experience with sulphazotised salts, it gives up this water very slowly. We further find that at 120° it slowly increases in weight again by re-taking water from the atmosphere and in doing so becomes hydrolysed and acid. When the hydrated salt is rapidly raised to, and maintained at 120°, such hydrolysis also occurs and thus fixes the water, causing the salt to suffer scarcely any change in weight.

The results of our determinations of sulphur and potassium agree with those got by Raschig, but with the potassium a little lower than the calculated number. As our methods of getting our preparations were somewhat exceptional, we submit the results of our analyses along with those got by the other investigators, also interesting from the peculiarities noticed of their agreements and variations :—

	Calc.	*Fremy.*	*Claus.* Mean.	*Raschig.* Mean.	*Divers and Haga.* (*a*)	(*b*)	(*c*)
Potassium ...	32·89	32·0	33·6	32·8	32·38	32·41	32·04
Sulphur	21·53	22·2	22·4	21·4	21·43	21·23	21·19
Nitrogen......	4·71	4·4	4·9	—	—	—	—
Oximide res.	10·27	—	—	—	9·05	—	10·23
Water.........	2·97	—	—	—	3·00	3·29	—

Sample (*a*) was prepared by adding to a cold supersaturated solution of dipotassium oximidosulphonate the calculated quantity of potassium hydroxide in solution, and leaving to crystallise. Sample (*b*) was prepared by dissolving the tripotassium salt in warm water and crystallising out. Sample (*c*) was obtained on adding potassium chloride to dipotassium-oximidosulphonate solution and then excess of ammonia.

Dipotassium oximidosulphonate and potassium nitrate.

Dipotassium oximidosulphonate unites with potassium nitrate, but not with sodium nitrate or with sulphates. Again, it unites with sodium chloride but not with potassium chloride.

The potassium-nitrate compound is obtained when a cold saturated solution of potassium nitrate is mixed with a warm concentrated solution of dipotassium oximidosulphonate. The compound begins almost at once to crystallise out in long silky needles, which by their abundance and by interlacing often make the mixed solutions set. Drained on a tile, the compound proved to be the simplest double salt of the two radicals, $K_2HNS_2O_7$, KNO_3, H_2O. Two preparations were analysed :—

	Calc.	(*a*)	(*b*)
Potassium.........	30·15	30·86	—
Sulphur............	41·24	41·52	41·83
Nitrogen	7·22	6·83	—

Heated, it explodes giving off much red fume. Water decomposes it into its component salts. Its reaction to litmus is neutral.

Dipotassium oximidosulphonate and sodium chloride.

The compound of the dipotassium salt with sodium chloride is obtained by dissolving the finely powdered potassium salt in cold saturated solution of sodium chloride. Operating sufficiently quickly, 35–40 ccs. of the salt solution may be made to dissolve nine grams of the potassium salt before the compound begins to crystallise out. The compound salt forms small striated good crystals belonging to the orthorhombic system, and is neutral to litmus. Two preparations were analysed and gave results agreeing with the formula—$5K_2HNS_2O_7$, $8NaCl$, $3OH_2$, but as water decomposes the compound into indefinite potassium-sodium oximidosulphonates and chlorides of both metals, this formula can only claim to be the simplest expression of the composition (see further p. 63).

	Calc.		(*b*)
Potassium	20·89	20·83	—
Sodium	9·86	9·73	—
Sulphur	17·14	17·32	—
Chlorine	15·21	14·96	14·90
Mixed sulphates ...	76·87	76·50	76·60

Potassium sodium oximidosulphonates.

It is perhaps not impossible, but it is certainly difficult to obtain potassium-sodium oximidosulphonates of very simple composition. Nor is it generally easy to get a salt of the same composition again and again. The salts now to be described must be regarded as examples only of an apparently indefinite number possible to prepare.

Most of them occur only in very small crystals, sometimes microscopic, generally aggregated in hard crusts and nodules. They were all however obtained in transparent though minute prismatic crystals, and under the microscope appeared to be homogeneous.

Normal sodium potassium salt.—Our attempts to produce normal mixed salts by adding the hydroxide of one metal to a hydrogen oximidosulphonate of the other metal have been unsuccessful. With any great excess of alkali, evaporation leads to the destruction of the oximide and crystallisation of potassium sulphite. With moderate excess of alkali and evaporation *in vacuo*, uncrystallisable or nearly uncrystallisable solutions are obtained. Such mixtures also fail for the most part to give a solid precipitate with alcohol ; at most, liquid droplets form which then sometimes slowly solidify to granules of microscopic crystals. Besides this, sodium oximidosulphonate in presence of alkali is largely soluble in strong spirit. When the alkali is used in only slight excess, salts are formed on evaporation, but these generally fall short of normal salts in composition. However, from the two single normal salts we did succeed in getting a mixed normal salt nearly pure, which we now describe.

This *mixed normal salt*, $2Na_3NS_2O_7$, $3K_3NS_2O_7$, $2H_2O$, but with one-fourth of the water replaced by its equivalent of potassium hydroxide, was obtained by evaporation in the desiccator of a solution of normal sodium and normal potassium oximidosulphonates in molecular proportions together with a little sodium and potassium hydroxides also in molecular proportions to each other. The salt appeared as a powdery deposit of microscopic crystals, and was drained dry on a tile, out of free contact with air. Reference to the description of the normal potassium salt, as obtained both by Raschig and by ourselves, will show that the small excess of potassium in the mixed salt is not peculiar to this preparation. Potassium and sodium were estimated by the Finkener-Dittmar method. The calculation A is for the true normal salt; B for the salt with the small excess of potash mentioned above :—

	Calculated.		Found.
	A	B	
Potassium	23·85	24·85	24·89
Sodium..............	9·35	9·23	9·40
Sulphur	21·68	21·40	21·35

A seven-eighths-normal potassium sodium salt, $K_{18}Na_3H_3(NS_2O_7)_8$, $20H_2O$, in nodular masses of minute transparent prisms was obtained on evaporating in a vacuum-desiccator a solution of the five-sixths-normal potassium salt with sodium hydroxide in quantity calculated to form normal salt. The composition of this salt is not very far removed from that of a much simpler mixed eight-ninths-normal salt, $K_7NaH(NS_2O_7)_3$, $8H_2O$, corresponding to the eight-ninths sodium salt, but the deviation is a little beyond the probable errors of analysis. In the table, the calculated numbers marked A are for the 'eight-ninths' formula, and those marked B for the 'seven-eighths' formula.

	Calculated.		Found.
	A	B	
Potassium..............	27·05	26·51	26·58
Sodium	2·27	2·59	2·49
Sulphur	18·98	19·28	19·22
Nitroxy-radical, NO.	8·90	9·03	9·01

A six-sevenths-normal potassium sodium salt, $K_2Na_{16}H_3(NS_2O_7)_7$, $5H_2O$, was obtained in some quantity by the evaporation of a solution of disodium oximidosulphonate to which a small proportion of potassium hydroxide and, unintentionally, some sodium hydroxide also had been added. It formed as a hard crust of small prisms on the bottom of the vessel. Attempts to prepare this salt again were unsuccessful;

the products then obtained will be noticed a few paragraphs later on. Preserved for many months, the salt was again examined, to confirm the results first obtained.

This salt scarcely loses weight in the vacuum-desiccator, although it contains water ; is not so freely soluble in water as are other potassium-sodium oximidosulphonates rich in sodium ; and may be recrystallised from solution almost unaltered. The analysis marked (*a*) is of the original preparation, and that marked (*b*) of the recrystallised salt :—

	Calc.	(*a*)	(*b*)
Potassium..............	4·17	4·10	4·27
Sodium.................	19·69	19·43	19·79
Sulphur	23·97	23·75	23·84
Nitroxy-radical, NO.	11.24	—	10·81

A five-sixths-normal potassium sodium salt, $K_{15}Na_5H_4(NS_2O_7)_8$, $9H_2O$, or not very far from the five-sixths normal monosodium salt, $K_4NaH(NS_2O_7)_2$, $2H_2O$, may from its mode of preparation possibly not be a single salt, yet is interesting on account of the way in which it was obtained, and for its relation in composition to the salt next described.

When the dipotassium salt was mixed with the calculated quantity of sodium hydroxide and the solution evaporated to a small bulk over sulphuric acid, no salt separated, and when alcohol was added, there occurred only a formation of droplets on the bottom of the vessel. But gradually these solidified to masses of minute crystalline particles having the composition formulated above instead of that of a normal salt or mixture of normal salts as it would have had if compounds of either metal had alone been present.

The calculation A is for the simpler and B for the more complex formula, given above :—

	Calculated.		Found.
	A	B	
Potassium...............	26·23	24·57	24·66
Sodium..................	3·86	4·82	4·93
Sulphur	21·46	21·44	21·37

The five-sixths-normal monopotassium sodium salt, $KNa_4H(NS_2O_7)_2$, H_2O, is nearly represented by two salts obtained in different ways. Both salts were however slightly more basic than calculated, while in the first to be noticed the potassium was slightly replaced by sodium, and in the second salt the sodium was slightly replaced by potassium, as will be seen from the numbers given. The first salt (*a*) was in small well-formed prismatic crystals, and was got accidentally by the spontaneous evaporation of an ammoniacal solution of disodium oximidosulphonate containing some potassium chloride. It was readily soluble in water but could not be recrystallised unchanged. It was free from chlorine. The second salt (*b*) was obtained in one of the attempts to get again the six-sevenths mixed salt already described. To seven molecules of disodium oximidosulphonate in solution were added two of sodium hydroxide and two of potassium hydroxide. The solution was then evaporated *in vacuo* until crystallisation occurred :—

	Calc.	Found.	
		(*a*)	(*b*)
Potassium...............	7·36	6·89	7·61
Sodium..................	17·36	17·69	17·25
Sulphur	24·15	23·93	23·96

A five-sixths-normal potassium sodium salt, $K_{1·4}Na_{3·6}H(NS_2O_7)_2,H_2O$, was obtained as a crust of microscopic orthorhombic prisms when a mixture in unknown proportions of disodium oximidosulphonate in solution and potassium hydroxide was evaporated in the desiccator.

A salt differing only a little in composition from this was obtained in another attempt to form the 'six-sevenths' mixed salt. In this case one molecule of dipotassium, two of disodium, and four of trisodium oximidosulphonates were brought together in solution and evaporated in the desiccator. The solution became somewhat viscid and only yielded a crystalline deposit when stirred with a glass rod. The deposit or precipitate was thoroughly drained on a porous tile, dissolved in a little water, and the solution evaporated to crystallisation. A salt now formed as a crust on the bottom of the vessel and resembled the salt sought for, from which however it differed materially in composition. The results of analysis of this preparation are given under (*b*), and those of the other preparation under (*a*). This is closely five-sixths normal, while (*b*) is a little less basic, and in other points deviates a little from the calculation :—

	Calc.	Found.	
		(*a*)	(*b*)
Potassium	10·20	10·16	9·71
Sodium	15·43	15·46	15·83
Sulphur	23·86	23·82	24·27
Alkalinity as sodium	4·29	4·29	4·30

Raschig's *potassium sodium sulphazotate* is a salt a little less basic than that just described as (*b*). He represents it as being—in the nomenclature of this paper, that is,—the *five-sixths normal monosodium oximidosulphonate*, $K_4NaH(NS_2O_7)_2$, $2H_2O$, and was justified in doing so by his analysis. But from his results, the salt would nevertheless appear to have had a composition approaching more nearly that of a *four-fifths normal* salt than of a *five-sixths normal* one, and hence in the order of basicity of these potassium sodium salts stands between that last described and that to follow.

Raschig describes the salt as forming opaque spherical masses of the size of millet seeds, and therefore resembling some of our preparations.

A four-fifths normal potassium sodium salt, $K_{2\cdot1}Na_{0\cdot3}H_{0\cdot6}NS_2O_7$, $0\cdot72H_2O$, was obtained by dissolving dipotassium oximidosulphonate in sodium-chloride solution and then adding ammonia in excess (p. 35). It separated out as a precipitate of exceedingly minute prisms slightly opaque when viewed under the microscope. It was free from chloride and ammonia. The atomic ratio of the metals, it will be seen, is $Na : K_7$, and of the metals to the hydrogen as $(KNa)_4 : H$.

	Calc.	Found.
Potassium	28·06	28·08
Sodium	2·36	2·40
Sulphur	21·87	21·86

A four-fifths normal potassium sodium salt, but a little less basic, so as to be *nineteen-twenty-fourths normal*, $K_{3\cdot75}NaH_{1\cdot25}(NS_2O_7)_2$, $1\cdot8H_2O$, was obtained almost in the same way as the last. Dipotassium oximidosulphonate in fine powder was dissolved in such quantity in a saturated solution of sodium chloride that crystallisation of an oximidosulphonate-chloride (p. 57) took place. This salt was redissolved by warming in its mother-liquor to which some ammonia water had been added, and the solution set aside. On cooling, the above salt crystallised out in minute prisms, which in a good vacuum over sulphuric acid lost nothing, although they contained water. The salt was free from chlorine and ammonia.

	Calc.	Found.
Potassium	25·13	25·11
Sodium	3·94	3·92
Sulphur	21·94	21·95

A seven-ninths normal potassium sodium salt, $K_6NaH_2(NS_2O_7)_3$, $2H_2O$, forms hard crusts of small rhombic prisms, only moderately soluble in water, and recrystallisable unchanged. It is obtained from the dipotassium oximidosulphonate, which exchanges one-third of its hydrogen for sodium on treatment with either sodium hydroxide, or sodium carbonate, or sodium chloride with ammonia.

In working with sodium hydroxide some small excess of this may be used without affecting the composition of the crystals. Analysis (*a*) was made upon crystals prepared by adding NaOH to $2K_2HNS_2O_7$, that is, in the proportion calculated for the five-sixths normal salt.

The dipotassium salt dissolved in an excess of warm solution of sodium carbonate, gave on cooling the crystals of which (*b*) is the analysis.

Analysis (*c*) is of crystals obtained by dissolving together in warm water, $NaCl+2K_2HNS_2O_7$, and then adding concentrated ammonia-water in moderate quantity, and leaving to cool. The sodium chloride was, it will be seen, taken in small excess, namely, in the quantity calculated to produce the five-sixths normal salt. When the effect of a great excess of sodium chloride was tried, the result was less satisfactory, the crystals being then somewhat opaque and less definite in composition. As best prepared, this salt made by the use of sodium chloride, is somewhat less basic than a seven-ninths normal salt, being half-way, in composition, between this and a *three-fourths normal salt.*

	Calc.	Found.		
		(*a*)	(*b*)	(*c*)
Potassium	27·10	27·01	27.22	26·73
Sodium	2·66	2·53	2·50	2·62
Sulphur	22·18	22·00	22·08	22·27

Two-thirds normal potassium-sodium salt, $KNaHNS_2O_7$, $3H_2O$.—This salt, but slightly more basic from the presence of about $\frac{1}{20}$ of an atom of potassium in excess of that in the formula and being therefore a $\frac{28}{39}$ normal instead of $\frac{2}{3}$ normal salt, was obtained in long rhombic prisms of small size by dissolving up 5·2 grams of dipotassium salt (slightly alkaline) in 30ccs. of a saturated solution of sodium chloride and 5ccs. of water, by the aid of a gentle heat, and leaving the solution to cool :—

	Calc.	Found.
Potassium..............	12·70	14·62
Sodium.................	7·49	7·60
Sulphur................	20·85	20·87

Reaction between the dipotassium salt and sodium chloride gives also, as already described, p. 57, a double oximidosulphonate-chloride, besides other compounds allied to this and the salt just described. It is a reaction which requires fuller investigation than we have found time to make of it, and what follows is all we can add concerning it.

While from sodium oximidosulphonate and potassium chloride, potassium oximidosulphonate crystallises out nearly free from sodium, there is obtained from potassium oximidosulphonate dissolved in sufficient quantity in a hot concentrated but not saturated solution of sodium chloride, a crystallisation of oximidosulphonate, half potassium, half sodium. If the sodium-chloride solution is saturated and the potassium oximidosulphonate is dissolved in it in the cold, what appears to be a compound of these salts, already described, quickly separates. But if by the aid of heat more potassium oximidosulphonate is dissolved, the salt which crystallises out is what may be represented as sodium chloride in combination with potassium-sodium oximidosulphonate. And if in the mother-liquor of this salt, now containing sodium oximidosulphonate in place of some of its sodium chloride, potassium oximidosulphonate is again dissolved by heat, the crystals which form on cooling consist of an oximidosulphonate, more of sodium than of potassium, and with only very little sodium chloride along with it. We give an example of the composition of such a salt, which was obtained in good transparent small rhombic prisms:—

Potassium	7·45
Sodium	12·98
Sulphur	23·65*
Chlorine	0·63

The potassium is to the sodium as K : Na_3, plus a very little for the chlorine.

By dissolving dipotassium oximidosulphonate in a warm concentrated solution of disodium oximidosulphonate, it is practically certain from what precedes that a potassium-sodium salt would crystallise out. We regret we have no experience to record on this point.

Ammonium oximidosulphonates.

Hydroxy-lead oximidosulphonate (p. 80) yields at once, when shaken with enough solution of ammonium acid-carbonate to convert its lead to carbonate, a solution of normal ammonium oximidosulphonate almost pure. Barium oximidosulphonate may be used in place of the lead salt, but not being basic it requires the normal instead of the acid ammonium carbonate to be used with it. The solution smells mildly of ammonia, but in a closed vessel may be preserved unchanged. Heated with exposure to air, it becomes a solution of the diammonium salt, by loss of ammonia. Guarding against hydrolysis, to which this salt is very liable, by adding a drop of strong solution of ammonia occasionally so as to maintain its alkalinity, the solution of the diammonium salt may be evaporated on the water-bath to an exceedingly small volume without decomposing. If, now,

---

* This number is calculated, as the sulphur was lost.

the very concentrated solution be quickly evaporated cold over sulphuric acid, it is possible to get the *diammonium salt* in good prismatic crystals, very soluble in water. If instead, the solution is mixed with concentrated ammonia-water and evaporated in an ammoniacal atmosphere over solid potassium hydroxide, crystals of another very soluble salt are obtained, having an unconquerable tendency to climb the sides of the vessel and there exfoliate. These crystals slowly effloresce in the desiccator, and occur in masses of overlapping flat prisms. They are believed to be the *five-sixths normal ammonium oximidosulphonate*, corresponding to Fremy's basic potassium sulphazotate.

We have no analyses to bring forward. The diammonium salt has hydrolysed before it could be freed from its mother-liquor. The alkaline salt has also not been obtained in quantity in such definite form as to promise results of value from its quantitative analysis. Heated, this salt decomposes like other oximidosulphonates suddenly, and leaves a residue of ammonium acid sulphate.

On evaporating a solution of normal ammonium oximidosulphonate with ammonium acetate over a water-bath, ammonia escaped as usual and the concentrated solution on cooling yielded a magma of lustrous needles. This magma slowly drained itself dry on the tile and for days evolved strong acetic-acid vapour without the oximidosulphonate hydrolysing or the compact dry mass losing its silky lustre. In the course of weeks, however, hydrolysis occurred and the mass became loose opaque crystals of ammonium hydrogen sulphate. It thus seems that diammonium oximidosulphonate like the potassium salt combines with other salts such as ammonium acetate.

Barium oximidosulphonates.

Barium chloride does not precipitate a solution of dipotassium or disodium oximidosulphonate, but the mixed solutions are very unstable, soon hydrolysing into sulphate and oxyamidosulphonate (*cf.* Claus). From the normal potassium or sodium salt it precipitates barium oximidosulphonate, in combination always with some potassium or sodium oximidosulphonate, and with very much when the alkali salt is in concentrated solution and kept in excess. The alkali salts intermediate to the normal and two-thirds normal salts behave towards barium chloride as mixtures, the two-thirds normal alkali salt remaining unprecipitated except in concentrated solutions when much of it, if the potassium salt, becomes insoluble in combination with the barium salt. The precipitates dissolve to some extent in warm concentrated solutions of the normal and two-thirds normal alkali oximidosulphonates but, for the most part, separate on cooling, sometimes richer in alkali salt.

Barium hydroxide precipitates solutions of the two-thirds normal as well as normal salts, and all the precipitates are combinations of barium with potassium or sodium salts. When the hydroxide is used in excess, and when barium chloride is used in excess with the normal or the intermediate salts, the precipitates are generally basic, that is, have some of the barium as hydroxide.

Ammonium oximidosulphonates behave much like the potassium and sodium salts, but have a much larger solvent action upon the barium precipitates. We have made no analyses of the ammonium barium salts.

There are apparently three barium salts $Ba_3(NS_2O_7)_2$, $BaHNS_2O_7$, and $(HOBa)_2HNS_2O_7$ or $(HOBa)BaNS_2O_7$; of which, however, the second is so unstable as to be known only in solution, while the third is known only in combination.

Normal barium oximidosulphonate, $Ba_3(NS_2O_7)_2$, $4H_2O$ and $8H_2O$.—The precipitate obtained by using barium chloride or hydroxide in excess with a potassium or sodium oximidosulphonate is washed and then nearly all dissolved by adding dilute hydrochloric acid with continual stirring until a solution is obtained neutral or only slightly alkaline to litmus. The turbid solution is as quickly as possible filtered, by vacuum-pump, into excess of warm baryta-water. The precipitate thus obtained when washed with boiled-out water, hot or cold, is the normal barium salt free from alkali and from carbonate. It is a voluminous curdy precipitate at first, but generally changes to a denser powder, crystalline under the microscope but to the naked eye chalk-like when dry. It is practically insoluble in water, but soluble in ammonium chloride. It is fully decomposed in the cold by ammonium or sodium carbonate solution. Heated dry, it suddenly decomposes into barium sulphate and gases. It loses water at common temperatures in dry air, and nearly all at 110°. Its composition, calculated and found, is shown by the following table, in which A refers to one preparation with 4 Aq., and B to another with 8 Aq. :—

	A		B	
	Calc.	Found.	Calc.	Found.
Barium	47·62	47·50	43·96	43·74
Sulphur	14·83	14·80	13·69	13·46

Two-thirds normal barium oximidosulphonates, $BaHNS_2O_7$, can be obtained in solution by adding just enough acid to the normal barium salt. When the normal salt is free from alkali and the acid is sulphuric the solution filtered is pure. When the normal barium salt is combined with any potassium or sodium salt the solution obtained by means of an acid is treated as described for getting the pure normal salt, which is then again converted to the two-thirds normal salt by sulphuric acid. The solution of this salt is distinctly acid to litmus and hydrolyses too readily to admit apparently of crystallising out the salt from it.

Barium sodium oximidosulphonates.—A normal one-fifth sodium salt, $Ba_6Na_3(NS_2O_7)_5$, $7H_2O$, is obtained when to normal sodium oximidosulphonate in strong solution, one mol., there is added barium chloride, one mol. It was also obtained by adding baryta-water to a strong solution of the normal sodium salt kept in excess. The precipitate unwashed or slightly washed is dried on a porous tile. It loses only one-third of its water at 120°. (*a*) was obtained from barium chloride and (*b*) from barium hydroxide :—

	Calc.	Found.	
		(*a*)	(*b*)
Barium...........	41·79	42·02	42·24
Sodium	3·51	3·60	3·44
Sulphur	16·27	15·69	15·97

Another normal, only one-seventh sodium, salt, $Ba_9Na_3(NS_2O_7)_7$, $7H_2O$, can be obtained by adding baryta-water to a mixed solution of one mol. of disodium salt and one mol. of barium chloride, and in other ways. (*a*) and (*b*) were separate preparations :—

	Calc.	Found.	
		(*a*)	(*b*)
Barium...........	44·71	44·70	44·18
Sodium	2·50	2·40	2·47
Sulphur	16·24	15·83	—

A normal salt richer in sodium was got from 3 mols. of trisodium and 3 mols. of disodium salt ground together with hardly enough water to dissolve all, by adding to the mixture very gradually and with trituration a dilute solution of one mol. of barium chloride, half of which was added before it caused any precipitation in the now dissolved salts. The mixture quickly thickened to a nearly opaque firm jelly which after a time broke up into a thoroughly liquid mixture of a powdery precipitate and an abundant mother-liquor. The precipitate was drained on a tile, and then had changed from a powder to a horny hard mass.* This was ground fine in a mortar and dried in a good desiccator, the grinding being once or twice repeated. Analysed it proved to be $BaNaNS_2O_7, H_2O$ with a little $Ba_3(NS_2O_7)_2, 9H_2O$:—

	$Ba_{18}Na_{15}(NS_2O_7)_{17}, 24H_2O$.	Found.	
Barium…………	38·10	38·36	38·01
Sodium ………	5·33	—	5·25
Sulphur ………	16·81	—	16·72

Barium potassium oximidosulphonates.—The normal potassium salt decomposes so quickly in aqueous solution into the five-sixths normal salt and potassium hydroxide that constant and simple results would probably not be obtained with it as a precipitating agent. We have used, as Fremy did, the K_5 salt, or with baryta the K_2 salt.

The seven-ninths normal salt, $Ba_3K_8H_4(NS_2O_7)_6, 9H_2O$, is obtained as a crystalline powdery precipitate when a concentrated solution of barium chloride, two mols., is added to three or more mols. of the five-sixths normal potassium salt in warm concentrated solution, this salt, it should be remembered, being very little soluble in cold water. The precipitate first formed redissolves in its mother-liquor up to the point when only half the barium chloride has been added, but is all again precipitated on adding the rest of the barium chloride and letting the mixture cool. The mother-liquor must be decanted soon and the precipitate drained on a tile, because the former in about an hour after cooling begins to deposit potassium salt. The results of the analysis of the precipitate were—

---

* The behaviour of the mixture in gelatinising and in breaking up then into a thin liquor and a precipitate which became horny on drying, is much like that of one of Fremy's potassium salts, his *metasulphazate*.

	Calc.	Found.
Barium	20·25	20·40
Potassium	15·41	15·66
Sulphur................	18·92	18·25

The sulphur, it will be seen, is a little low for the formula, a deviation attributable perhaps to the presence of a little K_5 salt from the mother-liquor.

In this salt the oximidosulphonate exists one-third as normal barium salt and two-thirds as dipotassium salt. In its formation the K_5 salt behaves, as usual, as mixed normal and dipotassium salts, of which one part of the former suffers decomposition with the barium chloride and the other remains in solution, while the dipotassium salt precipitates in combination with the barium salt:—

$$4K_5H(NS_2O_7)_2 + 3BaCl_2 = Ba_3(NS_2O_7)_2, 4K_2HNS_2O_7 + 2K_3NS_2O_7 + 6KCl.$$

On adding to a warm concentrated solution of three mols. of the K_5 salt, one mol. of barium chloride, agitating to redissolve the precipitate and then letting the solution cool, a relatively very large quantity of crystalline powdery precipitate is obtained, which from its quantity must consist largely of potassium salt. Being uncertain concerning its freedom from separate potassium salt we have not analysed it. It can be redissolved in its warmed mother-liquor and recovered by cooling, again and again. But if the mother-liquor decanted is allowed to stand some hours to deposit most of its potassium salt and then re-decanted on to the barium precipitate it fails to dissolve this when warmed with it, though it effects great change in its composition, dissolving out potassium salt. Thus treated, the precipitate was found to differ only a little from a salt having the formula $BaKNS_2O_7, H_2O$ and could be regarded as this salt retaining unchanged a little of the salt from which it had been prepared. It had the composition expressed by the formula, $Ba_{12}K_{14}H(NS_2O_7)_{13}, 10H_2O$:—

	Calc.	Found.
Barium	33·95	33·93
Potassium	11·35	11·57
Sulphur	17·18	17·03

The attempt to get the salt $BaKNS_2O_7$ by direct reaction thus:—

$$K_5H(NS_2O_7)_2 + BaCl_2 = BaKNS_2O_7 + K_2HNS_2O_7 + 2KCl.$$

was only partly successful. The precipitate obtained on adding to a warm concentrated solution of one mol. of the K_5 salt one of barium chloride had the composition shown by the formula $(HO)_2Ba_6K_4H(NS_2O_7)_5$, H_2O, or quite probably, $HOBa_6K_4(NS_2O_7)_5$, $2H_2O$. This composition would agree with that of a barium sodium salt already described, $Ba_6Na_3(NS_2O_7)_5$, if an atom of barium were not half displaced by one of potassium.

	Calc.	Found.
Barium	41·49	41·68
Potassium	7·89	8·22
Sulphur	16·15	16·06

This precipitate may be represented as a mixture or compound of $4BaKNS_2O_7$ with $(HOBa)_2HNS_2O_7, H_2O$ (see the lead salts 3, p. 81, and 7, p. 85) and it is probable that the precipitate first formed consists largely of the latter salt, and that when, by the accumulation of dipotassium salt the mother-liquor lessens in basicity, the BaK salt alone precipitates. The reaction representing the formation of the hydroxy-barium salt—

$$2BaCl_2 + 2K_3NS_2O_7 + 2H_2O = (HOBa)_2HNS_2O_7 + K_2HNS_2O_7 + 4KCl$$

—in which $(HOBa)_2HNS_2O_7$ when doubled is equivalent to $Ba(OH)_2 +$

$Ba_3(NS_2O_7)_2+H_2O$, shows the normal sodium salt behaving with a salt of barium somewhat as it does with zinc, manganese, copper, and other salts, that is, as dipotassium salt and potassium hydroxide (p. 47).

Fremy, by treating the K_5 salt with barium chloride, got a precipitate, gelatinous at first, afterwards crystalline, the composition of which, as given by him, may be expressed (1) pretty closely by $(HO)_3Ba_8K_8(NS_2O_7)_7$, or (2) by $BaKNS_2O_7$ as an approximation sufficiently near to Fremy's analytical results, considering the liability to impurity of his preparations, and his imperfect methods of analysis :—

	Calculated.		Found.
	(1)	(2)	(Fremy)
Barium............	39·29	37·43	39·90
Potassium.........	11·19	10·65	11·55
Sulphur	16·07	17·49	15·80

He must have kept the potassium salt in excess when precipitating. He found that baryta-water gave the same salt. Although much reliance cannot, we admit, be placed on Fremy's analytical results as closely accurate, we are not inclined to adopt the simpler formula rather than the other of the two we have calculated ; for our own results, here and in the case of strontium and lead salts, where we have been sure of the comparative purity of our preparations and accuracy of our methods of analysis, have taught us that compound oximidosulphonates are generally of complex composition. Claus, after experimenting for himself, pronounced Fremy's results to be worthless. He found that after ten minutes or so, the barium precipitates always began to decompose and to contain sulphate. We have not met with this difficulty, the barium salts (except the two-thirds normal salt, as already noticed) proving to be stable, and free from sulphate when analysed. As the barium salts when acidified are extremely rapidly hydrolysed, the best way to test their freedom from sulphate is to digest them with sodium carbonate, filter off and wash the barium carbonate, and observe whether this dissolves perfectly in nitric or hydrochloric acid.

Claus's experience may be accounted for by the presence of much dipotassium oximidosulphonate in the mother-liquor, which with barium chloride very rapidly yields sulphate by hydrolysis. He refused credence to Fremy's statement as to the formation of the dipotassium salt when the K_5 salt is precipitated by barium chloride and other salts, and consequently took no steps to protect himself against this accident.

On adding to a supersaturated solution of the dipotassium salt warm baryta-water not in excess, a precipitate was obtained by us somewhat poor in potassium; but then neither a supersaturated solution of the dipotassium salt nor a warm one of barium hydroxide is a solution of much concentration, which is the condition for the precipitate to contain much potassium. The composition of the precipitate agrees with that for the formula $Ba_9K_3(NS_2O_7)_7, 14H_2O$, matching which, except as to water, there is a barium sodium salt already described on a previous page:—

	Calc.	Found.
Barium	42·05	42.14
Potassium	4·01	4·19
Sulphur..............	15·28	15·32

Two mols. of dipotassium salt react with one mol. of barium hydroxide to yield $BaKNS_2O_7$, which is resolved by water into normal potassium salt and normal barium salt retaining a twelfth of the former, thus:—

$$18K_2HNS_2O_7+9Ba(OH)_2=Ba_9K_3(NS_2O_7)_7+11K_3NS_2O_7+18H_2O.$$

To show the effect of adding the barium hydroxide in greater quantity upon the normal potassium salt otherwise found in the mother-liquor, we may give the result of adding it in some excess to a warm solution of the K_5 salt. The precipitate obtained had a composition which may be regarded as resulting from the addition of barium hydroxide to the preceding salt, or as that of a hydroxy-derivative of that salt, in which half the barium is as half-hydroxide. The composition of the salt was $(HO)_3Ba_8K_2(NS_2O_7)_5$, $14H_2O$, which is nearly equivalent to $(HOBa)_6Ba_6K_3(NS_2O_7)_7$, $19\frac{1}{2}H_2O$, or $3Ba(OH)_2 + Ba_9K_3(NS_2O_7)_7$. It is also related to Fremy's salt, being that salt with K_5 replaced by $(HOBa)_3Ba$:—

	Calc.	Found.
Barium	45·17	45·29
Potassium	3·21	3·21
Sulphur..............	13·18	13·11

The reaction has been one in which potassium hydroxide is largely formed :—

$$5K_5H(NS_2O_7)_2 + 16Ba(OH)_2 = 2(HO)_3Ba_8K_2(NS_2O_7)_5 + 21KOH + 5H_2O$$

The mother-liquor was tested and found to contain much potassium hydroxide and some barium hydroxide and nothing else.

When barium chloride in slight excess and in moderately dilute solution is added to the K_5 salt, it yields a similar compound to that obtained by excess of baryta-water, but with some chloride in place of hydroxide of barium. The precipitate had the composition $Cl(HO)_2Ba_{12}K_3(NS_2O_7)_8$, $7H_3O$ or $BaCl_2 + 2Ba(OH)_2 + Ba_3(NS_2O_7)_2 + 2Ba_9K_3(NS_2O_7)_7 + 14H_2O$ (see lead salt 4, p. 82).

	Calc.	Found.
Barium	47·29	47·73
Potassium	3·37	3·24
Sulphur..............	14·73	14·67
Chlorine	1·02	0·96

Strontium oximidosulphonates.

We have not made a general examination of the strontium salts. What we have observed qualitatively and at variance with Fremy we have recorded on p. 48. On adding warm concentrated strontia-water to the five-sixths normal potassium salt the mixed solutions remain clear for a few moments, but then become suddenly filled with fine needles of very silky lustre. Yet this precipitate, which retains its lustre when dry, has a composition as complex as that of any barium salt we have examined, the formula for it being $(HO)_3Sr_{11}K_8(NS_2O_7)_9, 16H_2O$, which may be expressed more simply as $(HOSr)_3NS_2O_7, 8(SrKNS_2O_7, 2H_2O)$, and in other ways :—

	Calc.	Found.
Strontium	28·96	28·69
Potassium	9·39	9·39
Sulphur...............	17·33	17·41
Nitroxy-rad., NO,...	8·12	8·16
Water	8·44	8·67
Hydroxyl.............	1·53	—

A strontium sodium salt crystallises out in hemispherical tufts of brilliant silky needles, some hours after mixing either the disodium salt with warm concentrated strontia-water, or the normal sodium salt with strontium chloride. No analysis has been made of the salt.

Calcium oximidosulphonates.

Calcium salts, including calcium hydroxide, are not precipitated by alkali oximidosulphonates. When solution of the normal or the two-thirds normal ammonium salt is mixed with pure soft calcium hydroxide, one mol. of the salt dissolves about one mol. of the hydroxide, this not having been added in excess, and ammonia is liberated. The solution evaporated on the water-bath gives off ammonia and leaves a crystalline residue, which may be taken to be a compound or mixture of the salts $CaAmNS_2O_7$ and $CaHNS_2O_7$. Treated with water some nearly insoluble calcium oximidosulphonate is left, while the greater part of the mass dissolves up as calcium ammonium salt.

If after dissolving, as described in the preceding paragraph, two mols. of calcium hydroxide in two mols. of the ammonium salt, a third mol. of the softest moist calcium hydroxide be stirred in, it may be seen to give place to a voluminous precipitate which most probably is normal calcium oximidosulphonate. The precipitate has very little solubility in water, and is so free from ammonia as to evolve none when mixed with calcium hydroxide, a test however which is not quite conclusive.

Lead oximidosulphonates.

Reactions of alkali oximidosulphonates with lead acetates.—The reactions of oximidosulphonates with lead salts are complex. The disodium and dipotassium salts give no precipitate with normal lead acetate, but precipitate with the basic lead acetates. With highly basic acetates in good excess the precipitate is mainly or wholly the normal hydroxy-lead salt (numbered 2 in the description of these salts which follows). With a basic acetate not in excess and in solution not concentrated, the precipitate is the salt numbered 3; while with medium quantities of basic acetate and concentrated solutions the precipitate is approximately the salt 4. The precipitates usually contain, especially when strong solutions are worked with, acetate and alkali salt, only partially removable by washing with hot water.

Normal sodium oximidosulphonate and normal lead acetate show no immediate precipitation unless the solutions are dilute. With enough of the sodium salt present, two mols. or more, to one mol. of the acetate, and using concentrated solutions, the mixture in a few hours becomes filled more or less with a soft mass of minute crystals of a lead sodium salt (7). Using much less sodium salt the mixed solutions, if not dilute, also remain clear, but very slowly deposit spherical crystalline hard grains of the salt 4. The mother-liquor of this salt precipitates with water. If less concentrated the mixed solutions yield a precipitate at once, which however redissolves on heating, while concentrating the mixture by evaporation on a water-bath causes the precipitate in what were even dilute solutions, to gradually redissolve. Evaporation to dryness, yields a gum-like mass soluble in a little water but decomposed by much.

Normal potassium oximidosulphonate and also the K_5 salt give an immediate precipitate with normal lead acetate, soluble in excess of either mother-salt in strong solution, but the solution remains clear for only a few moments and then gives a crystalline precipitate unlike the flocculent and voluminous one first formed (*cf.* Fremy). When the oximide salt is in excess the precipitate is 6; with the acetate in excess it is 5. Normal ammonium oximidosulphonate is like the sodium salt in keeping clear for a long time after being mixed with normal lead acetate when in moderately concentrated solution, and in precipitating when largely diluted. Its behaviour has not been further observed.

The normal sodium salt and a basic lead acetate give no precipitate when the former is in the proportion of one mol. or more to one mol. of hemihydroxy-lead acetate, even after a long time or upon dilution with water. With the basic lead acetate in excess precipitation of the normal hydroxy-lead salt (2) is immediate.

The normal potassium salt in excess and in concentrated solution remains clear for a very short time after being mixed with basic acetate; it then deposits a crystalline flocculent precipitate redissolving on heating and re-forming on cooling (6). The basic acetate being in excess, instant precipitation takes place. The K_5 salt in excess with basic lead acetate behaves as with the normal acetate (*cf.* Fremy). With the basic acetate in excess it reacts in the same way as the normal potassium salt. The normal ammonium salt with basic lead acetate behaves essentially as the sodium salt, but the solvent action of ammonium salts prevents complete precipitation. Except when a basic acetate in excess is used, the mother-liquors of the lead precipitates are rich in the two-thirds normal salt of the alkali metal used, a fact pointed out by Fremy, but emphatically denied by Claus.

Description of the salts.—Like other oximidosulphonates the lead salts combine readily and in varying proportions with other salts. Accordingly, several double salts of lead and sodium, of lead and potassium, and even of lead and hydrogen can be prepared. These are partly decomposed by water, but washing even with hot water never removes all alkali salt. In nearly all the salts the lead is present half as hydroxide or oxide. An exception is the unstable two-thirds normal lead salt. With admissible and only slight qualifications, all the salts we have analysed may be expressed as derivatives of one, two, three, or four molecules of the acid.

(1) *Two-thirds normal lead oximidosulphonate*, $PbHNS_2O_7$. This salt can be obtained from the normal hydroxy-lead salt (2) which is insoluble in water, by stirring it with water containing almost enough sulphuric acid to deprive it of two-thirds of its lead. The mother-liquor, which is slightly acid, when moderately evaporated in the desiccator gives a crust of minute crystals. These appear under the microscope as transparent prisms somewhat hollowed at their middle to a dumb-bell-shape. The salt is only sparingly soluble, and is very unstable. We have not analysed it.

(2) *Normal hydroxy-lead oximidosulphonate*, $(HOPb)_3NS_2O_7$,

$3H_2O$.—Hemihydroxy or still more basic lead acetate in good excess of the calculated quantity yields this salt in the pure state when normal sodium oximidosulphonate is poured into it with stirring. When the lead solution is poured gradually into the sodium salt the precipitate contains generally a little lead hydroxide, free or combined. The salt is quite stable and may be freely washed with water hot or cold. It is a very voluminous flocculent precipitate, not in the least slimy or gelatinous, evidently crystalline under the microscope. The reaction by which it is formed is expressed by the equation—

$$Na_3NS_2O_7 + 3(PbOH)O\overline{Ac} = (HOPb)_3NS_2O_7 + 3NaO\overline{Ac}.$$

The salt can also be prepared, when sufficient care is taken, by adding to good excess of tribasic lead acetate a solution of the disodium salt. The reaction then is—

$$Na_2HNS_2O_7 + Pb_3(OH)_4(O\overline{Ac})_2 = (HOPb)_3NS_2O_7 + 2NaO\overline{Ac} + H_2O.$$

This lead salt decomposes when heated, as already described (p. 42) into sulphite and nitrite. It is soluble in acetic and other acids, in sodium hydroxide, in ammonium chloride and other ammonium salts, including ammonium oximidosulphonate. It is easily and fully decomposed in the cold by sodium, potassium, or ammonium hydrogen carbonate. The last named salt gives as an intermediate product a soluble lead ammonium salt (7). The results of analysis agree well with calculation :—

	Calc.	Found.
Lead	67·79	67·57
Sulphur..............	6·99	6·89

(3) *Two-thirds normal hydroxy-lead oximidosulphonate,* $(HOPb)_2HNS_2O_7, H_2O$.—Hemihydroxy-lead acetate added to a solution of dipotassium oximidosulphonate, the latter in small excess, gives a

precipitate of this salt, not quite pure however, but containing small quantities of potassium, acetic acid, and lead in excess. The corresponding sodium salt could no doubt be used in place of the potassium salt, but has not been tried. The precipitate is voluminous and flocculent. Its formation is represented by the equation—

$$K_2HNS_2O_7+2(PbOH)O\overline{Ac}=(HOPb)_2HNS_2O_7+2KO\overline{Ac}.$$

Analysis of a preparation freest from potassium gave the following results, which are compared with the results of calculation for the above formula with one-ninth of an atom of PbO additional:—

	Calc.	Found.
Lead	64·10	63·92
Potassium............	—	0·23
Sulphur	9·39	9·36

The slight approach in composition to the normal hydroxy-lead salt, which the small excess of lead indicates, is in agreement with what is observed in preparing the dipotassium salt, which is apt to crystallise with a little excess of potassium. Calculation for the pure salt gives lead 63·01 and sulphur 9·74 per cent.

(4) *Five-sixths normal aceto-hydroxy-lead oximidosulphonate,* $(\overline{Ac}OPb)(HOPb)_4H(NS_2O_7)_2$, $2\frac{1}{2}H_2O$.—When to two mols. of normal sodium oximidosulphonate in somewhat concentrated solution excess—say three to six mols.—of normal lead acetate is added, there form in some hours or days hard, almost opaque, spherical granules, of radiating crystalline structure, some at the surface of the solution, others adherent to the sides and bottom of the vessel. These granules are of the required salt not quite pure however and incapable of being purified because slowly decomposed by water. The preparation of which the analysis follows, contained, it will be seen, acetic acid in excess of that indicated by the formula. It would be possible to include this extra

eighth of acetic acid in a complex formula, but to do so would be almost vain, for while the acetic acid was in other preparations also in excess, the excess was variable though the total acetic acid was still about 4 per cent:—

	Calc.	Found.
Lead	65·18	65·10
Sulphur..............	8·06	8·14
Acetic acid	3·78	4·29

(5) *Five-sixths normal hydroxy-lead potassium oximidosulphonate,* $(HOPb)_5K_5H_2(NS_2O_7)_4$.—To form this salt calculation points to the use of 7 mols. of the K_5 salt and 5 mols. of normal lead acetate. It was obtained by us by taking 8 mols. to 6 mols. of the respective salts, the former in warm concentrated solution and the latter also in concentrated solution. Almost immediately after mixing them together a dense granular but still somewhat curdy precipitate separated, which was drained on a tile. Air-dried, it lost weight in a desiccator equal to 5·3 per cent.; the loss of $2H_2O$ would be about that. It was the dehydrated salt which was analysed. The equation expressing its formation is—

$$7K_5H(NS_2O_7)_2+5Pb(O\overline{Ac})_2+5H_2O=(HOPb)_5K_5H_2(NS_2O_7)_4+10KO\overline{Ac}$$
$$+10K_2HNS_2O_7.$$

This salt is somewhat soluble in its mother-liquor. On adding more of the potassium salt to the mother-liquor, a precipitate of apparently the salt next to be described formed.

	Calc.	Found.
Lead	49·79	50·04
Potassium...........	9·42	9·15
Sulphur..............	12·34	12·46

(6) *Eight-ninths normal oxy-lead potassium oximidosulphonate,* $(OPb_2)K_6H(NS_2O_7)_3$, or the *normal* salt $(HOPb)PbK_6(NS_2O_7)_3$.—Pro-

ceeding as for the last described salt, but taking to two mols. of the potassium salt only one mol. of the lead salt, the clear solution obtained after agitating to dissolve the precipitate first formed, yielded us when stirred with a glass rod a sandy crystalline precipitate of the composition expressed by either of the above formulæ, but with nearly $\frac{1}{16}$ of the potassium replaced by hydrogen, as the calculation shows :—

	Calc.	Found.
Lead	33·51	33·46
Potassium............	18·98	18·33
Sulphur..............	15·54	15·82

The mother-liquor proved to be free from lead and practically neutral. The following equation expresses, therefore, the reaction which had taken place :—

$$4K_5H(NS_2O_7)_2+2Pb(O\overline{Ac})_2+H_2O=OPb_2K_6H(NS_2O_7)_3+4KO\overline{Ac}$$
$$+5K_2HNS_2O_7.$$

Fremy's salt.—Almost in the same way, that is, by adding normal lead acetate drop by drop to warm concentrated solution of the K_5 salt, agitating to dissolve the immediate precipitate, and going on until suddenly a second crystalline precipitate appeared, Fremy got a salt having nearly the same content of sulphur as our salt just described, but with more lead and less potassium, which admits of no simple representation by a formula, although there are, closely enough, 4K to 1Pb. We give the calculation for $PbK_4(NS_2O_7)_2$, along with Fremy's finding :—

	Calc.	Found. (Fremy)
Lead	27·85	28·40
Potassium............	21·04	21·44
Sulphur..............	17·22	15·65
Nitrogen	3·77	3·48

from which it will be seen that his sulphur is about one-tenth too low for this formula, one which is besides improbable from the fact of the lead in it being wholly combined with the oximide radical.

(7) *Eight-ninths normal hydroxy-lead sodium oximidosulphonate*, $(HOPb)_2Na_6H(NS_2O_7)_3$, $14H_2O$.—Concentrated solutions of two mols. of the normal sodium salt and one mol. of normal lead acetate are mixed together and left, protected from the air, till crystallisation occurs, when the solution becomes filled, or partly filled, with minute crystals forming with it a soft magma. The crystals are drained from their mother-liquor and pressed between porous tiles. They are efflorescent and are dissolved and decomposed by water. Two quantities were prepared and analysed, the one more effloresced than the other. Calculation A is for 14 Aq. and B for 10 Aq. :—

	A		B	
	Calc.	Found.	Calc.	Found.
Lead	29·38	29·31	30·97	31·32
Sodium	9·79	9·69	10·32	10·05
Sulphur	13·63	13·73	14·36	14·35

This salt, like the potassium salt, can be formulated as a normal salt, $(HOPb)PbNa_6(NS_2O_7)_3$, $15H_2O$, or as an oxy-lead salt, $(OPb_2)Na_6H(NS_2O_7)_3$, but with water of crystallisation. The mother-liquor of the crystals contains much disodium oximidosulphonate :—

$$4Na_3NS_2O_7 + 2Pb(O\overline{Ac})_2 + 2H_2O = (HOPb)_2Na_6H(NS_2O_7)_3 + 4NaO\overline{Ac} + Na_2HNS_2O_7.$$

(8) *Normal diammonium hydroxy-lead oximidosulphonate*, $HOPbAm_2NS_2O_7$.—A normal salt with one atom of the hydroxy-lead radical to two of ammonium has not been isolated in the pure state, but can be got in solution almost pure, and the solution can be evaporated in a desiccator to dryness with the loss of a small fraction only of its ammonia. Normal hydroxy-lead oximidosulphonate (2) is pre-

cipitated from a known quantity of normal sodium oximidosulphonate, washed by decantation, and its last washing-water closely decanted. The precipitate even on long standing still occupies a large volume of liquid, and if to it there is now added powdered ammonium hydrogen carbonate in quantity calculated to decompose completely barely two-thirds of the lead salt and the mixture is well agitated and then left to stand, lead carbonate, filling a very small space, settles down and a clear mother-liquor can be decanted having only a scarcely noticeable odour of ammonia and containing one atom of lead to two of ammonium, practically all the oximidosulphonic radical, and no carbonic acid. Much water added renders it milky. It can be evaporated to dryness in the cold and the residue redissolved in water.

The disodium and dipotassium hydroxy-lead salts cannot be prepared in a similar way, but a solution of either of these salts, or of the diammonium salt, along with acetate, is apparently obtained by mixing together in concentrated solution one mol. of hemihydroxy-lead acetate and one mol. of normal oximidosulphonate of sodium, potassium, or ammonium. The solution dries up to a vitreous mass with a little confused crystalline matter, and is precipitated on dilution with water.

* * *