

**Identification and Constitution of Fremy's
Sulphazotised Salts of Potassium, his
Sulphazate, Sulphazite, etc.**

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A sufficiently concentrated solution of potassium nitrite and hydroxide submitted to the action of sulphur dioxide gave Fremy minute silky needles of a salt which he provisionally named *potassium sulphazate*. With slightly diminished concentration of the solution he generally obtained instead the brilliant, often hard, rhombic prisms of *potassium basic sulphazotate* (5/6-normal hydroximidodisulphate, this journal, 7, 15). But sometimes there was obtained neither of these salts before the solution became transformed into a starch-like jelly through the formation of a salt which he named *potassium metasulphazate*, or else became filled with spangles of yet another salt called by him *potassium metasulphazotate*. When the solution was a little too dilute to give any of these and when too much alkali had not been added, there usually appeared peculiarly pointed crystals of the salt he named *potassium neutral sulphazotate* (2/3-normal hydroximidodisulphate Raschig) and, lastly, with still greater dilution

the minute brilliant needles of his *potassium sulphammonate* (nitrilosulphate Berglund). Still other salts he believed to be produced in the first stages of the reaction between the nitrite and sulphur dioxide, one of which he named *potassium sulphazite*; but this he did not obtain directly, finding a reason for this in the exceeding solubility of this early formed salt. He prepared it—but only in quite small quantity and as crystalline warty granules—by the action of water upon the ‘sulphazate’ whereby this was converted into ‘basic sulphazotate’ which deposited and a solution that on evaporation yielded the ‘sulphazite.’ These two salts could together in solution be changed back into the ‘metasulphazotate’ while the ‘sulphazite’ and the ‘sulphazate’ could similarly often be changed into the ‘metasulphazate’ again. These two ‘meta’ salts he regarded therefore as perhaps merely double salts of the others. The ‘sulphazite,’ the ‘sulphazate,’ and the ‘sulphazotates’ he treated as being members of a series of salts in which there were two atoms of nitrogen from one up to eight atoms of sulphur,—three in the ‘sulphazite, four in the ‘sulphazate’, and five in the ‘sulphazotates.’ With this conception of the nature of these salts, based on his analyses, it was easy to understand the decomposition of the ‘sulphazate’ into the ‘sulphazite’ and the ‘sulphazotate.’ But this and other of Fremy’s interpretations of the facts observed by him have lost all importance and particular interest through the progress of chemistry since his memoir was published and only his account of the facts requires consideration now.

Subsequent work by others and ourselves in the same field has shown that Fremy in the account he gave of the preparation of his many salts went too little into details as to the conditions

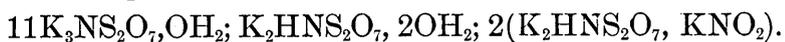
under which they were obtained,—apparently because he was not able to be more precise. When Claus attempted to get Fremy's salts he obtained only masses of minute crystals of salts of whose individuality and nature he could make out little because of the impossibility of dissolving them all up undecomposed. In his experiments the 'sulphammonate' (nitrilosulphate) was always formed in considerable quantity either as a first or secondary product and by its presence prevented any satisfactory investigation of the other salts. In Fremy's working, this most easily formed salt came only as the final product of the sulphonation and therefore gave him no trouble. Claus emphatically displayed his scepticism as to Fremy's results; yet in nearly every point in which he differed from Fremy as to the facts we find Fremy to have been right. When Raschig repeated Fremy's work—*but with the modifications in procedure introduced by Claus*—he got results similar to, though less unsatisfactory than, those Claus had obtained. He made an approach to Fremy's work in so far as that he often got very little nitrilosulphate; nevertheless he too failed in his attempts to prepare the 'sulphazate' in Fremy's way.

In perhaps all essential points we can lay down the method to repeat Fremy's experimental work successfully. But in some cases a little uncertainty obtains owing to the fact that the very concentrated and complex solutions which yield Fremy's salts are apt to deposit what is virtually the same salt in different forms as well as at times salts quite distinct from each other under only slight and obscure variations in the circumstances attending their formation.

Sulphazate.—This is Fremy's first salt directly obtained in his sulphonation of the nitrite. In getting it he took approximately 5 mols. potassium nitrite to 2 mols. potassium hydroxide and a little water and into the solution passed sulphur dioxide

until it became almost filled with silky needles very soluble in water. So far it is easy to follow Fremy with a full measure of success if only the water used is limited to perhaps twice the weight of the nitrite and that the heating effect of the nitrite is counteracted by cooling. Claus and after him Raschig failed but then inexplicably to us they did not start with Fremy's proportions of nitrite to hydroxide, though even with the proportions they took, success was possible with care. The salt thus formed by Fremy was not tested and analysed by him until after it had been changed (but without his having recognised the fact) by the further treatment to which he submitted it. Before its change it is potassium nitrito- $\frac{2}{3}$ normal hydroximidodisulphate described in the preceding paper, a neutral salt decomposed by water into its constituent salts. Fremy's finished 'sulphazate' was strongly alkaline and very caustic and when decomposed by water gave nitrite and the $\frac{5}{6}$ normal hydroximidodisulphate—not the $\frac{2}{3}$ -normal salt. Also the analysis he gave of it furnished numbers such as the original product could not have given him. Instead of potassium, 33.10, sulphur, 18.06, and nitrogen, 7.9 per cent., he got potassium, 34.90, sulphur, 19.55, and nitrogen, 4.9. We can learn what his after-treatment was by reference to other parts of his paper where he speaks of the care necessary (when sulphonating the nitrite) to maintain the alkalinity of the solution by adding potassium hydroxide from time to time and of dissolving sulphazotised salts for examination in water containing this alkali. Certain it is he must have added some potassium hydroxide to the solution after getting it to crystallise, as a precaution to preserve the salt. Now the effect of this addition is to change the composition of the product without much affecting its silky asbestos-like appearance. The change in com-

position is to deprive it of much of its nitrite and to convert the 2/3-normal into more nearly normal hydroximidosulphate—to replace, therefore, potassium nitrite by potassium hydroxide. Accepting Fremy's mean numbers as accurate, what he analysed had the composition,



	Potssm.	Sulphur	Nitrogen	Alk. potssm.
Found,	34.9	19.55	4.9	— per cent.
Calc,	34.9	19.51	4.9	9.36 „

But his analyses have no claim to receive such close treatment, his nitrogen seemingly being always much too low; and it is sufficient to say of his 'sulphazate' that it was the silky asbestos-like nitrito-2/3 normal hydroximidosulphate more or less converted into the also silky asbestos-like normal hydroximidosulphate, an account of it with which Fremy's description of its other properties entirely agrees. With dilute acids it gave slowly nitrous oxide unmixed with nitric oxide. Fremy specially points out that no *sulphazic acid* or any other *sulphazates* could be obtained from the potassium salt. There is, therefore, nothing to justify belief in this compound being the salt of a particular single acid, the *sulphazic*.

Sulphazite.—What Fremy named *potassium sulphazite* he only once obtained, and then not by direct sulphonation of the nitrite, in the form of white mammillated crystalline crusts from a solution thickened by the other salts contained in it. That is, to say, his *sulphazate* when dissolved in a little water containing some potassium hydroxide deposited crystals of *basic sulphazotate* (5/6 normal hydroximidosulphate), and left a mother-liquor which on cold evaporation till syrupy yielded the sulphazite. It showed great analogy with his *sulphazate* but was distinguished from it

by having little tendency to hydrolyse and by at once evolving some nitric oxide when its solution was mixed with a dilute acid. Water decomposed the *sulphazite*, but into what products was not ascertained.

We have sufficiently realised Fremy's expectations that his sulphazite might directly result from sulphonating the nitrite with subsequent addition of alkali. The substance obtained in this way did not differ greatly in composition from his :

	Potassm.	Sulphur
Fremy's salt,	38.16	16.27 per cent.
D. & H's salt,	36.94	16.37 ,,

and agreed with it in chemical properties, so far as is known. At the same time it was indistinguishable from a compound of nitrite with $5/6$ normal hydroximidodisulphate, and has been described by us as such in the preceding paper (p. 218) in which it stands as the third of these double salts and in which its preparation is given. Other experiments of various kinds have yielded us such 'mammillated crusts' as Fremy got, which, though only in rough agreement in percentage composition with his sulphazite, behaved like it and proved to be impure double salts of nitrite with $5/6$ normal or more nearly normal hydroximidodisulphate. We are therefore convinced that his sulphazite was only such a double salt.

Metasulphazate.*—In Fremy's experience it sometimes happened, when passing sulphur dioxide into solution of nitrite and alkali of a concentration intermediate to that giving *sulphazate* and that giving *basic sulphazotate*, the solution set to a starch-like jelly instead of crystallising. He obtained a similar jelly by cooling

* Often, misprinted *metasulphazotate* in the French original, but not in the German translation.

a concentrated solution of *sulphazate* and *sulphazite*; also by boiling a solution of *sulphazate* and then cooling it. When strongly compressed the jelly became a transparent wax-like mass. Heated in this waxy state to 50°-60° it suddenly changed into a solution of *sulphazite* and minute crystals of *basic sulphazotate*. In all other respects it proved to be intermediate in properties to *sulphazate* and *sulphazite*. No other *metasulphazates* could be prepared from it, so that Fremy was disposed to regard it as being a double salt of *sulphazate* and *sulphazite*. Its constitution must therefore have been that of nitrite combined with normal or 5/6 normal hydroximidosulphate in such proportions and with such additions perhaps of alkali as prevented crystallisation.

We have not had Fremy's success in getting this salt in form of jelly and wax but have met with just such phenomena when forming barium sodium hydroximidosulphate, $\text{BaNaNS}_2\text{O}_7$, OH_2 , as will be found described in our paper already frequently referred to. We have however obtained a salt, or homogeneous mixture of salts, of the same composition as the *metasulphazate*, but with the form of the silky radiating fibrous crystals of the nitrito-normal hydroximidosulphate, from which it differed only in showing deficiency of nitrite, that is, it was equivalent in composition to a mixture of the normal salt and its nitrite compound, both of which crystallise with the same habit. We give below Fremy's numbers, our own, and those calculated for the expression, $3(\text{KNO}_2, 2\text{K}_3\text{NS}_2\text{O}_7, 4\text{OH}_2); \text{K}_3\text{NS}_2\text{O}_7; 3\text{OH}_2$.

	Potssm.	Sulphur	Nitrogen	Alk. potssm.
Found (Fremy),	35.10	16.74	4.81	— per cent.
„ (D. & H.),	35.10	16.68	—	10.47 „
Calculated,	35.06	16.74	5.23	10.23 „

We got the salt by dissolving the hydroximidosulphate in

hot concentrated nitrite solution containing alkali. To 100 cc. water there were present $45\frac{1}{2}$ grm. nitrite and $1\frac{2}{3}$ grm. potassium hydroxide; for 66 mol. nitrite there were dissolved 10 mol. anhydrous normal hydroximosulphate. But for the salt being in beautiful asbestos-like fibres, there was nothing to distinguish it from the jelly and the wax-like *metasulphazate*, which, therefore, we do not hesitate to class as a nitrito-hydroximosulphate.

Basic sulphazotate, which Fremy considers next, has been shown by us already (*loc. cit.*) to be the $\frac{5}{6}$ normal hydroximosulphate, and not the salt of a distinct acid, the *sulphazotic*. It is liable to contain a small excess of potassium when crystallised from a strongly alkaline solution. A solution of the normal salt readily deposits it, as does also that of the nitrite compound of the normal salt.

Neutral sulphazotate was shown by Raschig to be the $\frac{2}{3}$ normal hydroximosulphate. The *potassium sulphazotates* were distinguished by Fremy from the salts previously described by him by their ability to form other sulphazotates by double decomposition. Fremy's analytical results in the case of the *neutral sulphazotates* are hopelessly out of accord with its constitution and properties, though those for the *basic sulphazotate* are satisfactory enough.

Sulphazidate, produced by the hydrolysis of the *sulphazotate*, is hydroxyamidiosulphate (Claus). *Sulphazilate* and *metasulphazilate*, oxidation products of *sulphazotate* are $\text{ON}(\text{SO}_3\text{K})_2$ and $\text{ON}(\text{SO}_3\text{K})_3$, and have been studied by Claus, Raschig, and Hantzsch.

Metasulphazotate.—Sometimes Fremy got a salt in the form of spangles (*paillettes*), in appearance like minute crystals of *basic sulphazotate*, but differing from these in not being hard under pressure. This salt he named, therefore, *metasulphazotate*. According

to him it is also obtainable by mixing (hot) solutions of the (*basic*) *sulphazotate* and *sulphazite*. It is very soluble in water, very alkaline and unstable unless the water contains alkali. In pure water it becomes *basic sulphazotate* and *sulphazite* again. It shows the greatest analogy with *metasulphazate* and is distinguished in the same way as this salt from *basic sulphazotate*. It may be a compound of *basic sulphazotate* and *sulphazite*. So far Fremy. It will be evident that there is nothing in its history or properties to distinguish it, except its occurring in the form of sparkling particles and even that can be met with in the *basic sulphazotate* suddenly precipitated; we have also got other of the sulphazotised salts in what may be called spangles, though not this particular salt. In the preceding paper, page 214, we have described an impure form of nitrito-2/3 normal hydroximidodisulphate obtained by dissolving the 5/6 normal salt in a hot concentrated solution of nitrite, but still not so very concentrated as to give the nitrito-5/6 normal double salt. This preparation is lustreless while in its mother-liquor, but when dried on the tile has a fine silvery lustre. It has when dried in the desiccator exactly the composition of Fremy's *metasulphazotate* and is much less alkaline than the *metasulphazotate* and is much less alkaline than the *metasulphazate*. It may be formulated as



	Potssm.	Sulphur	Nitrogen	Alk. potssm.
Found (Fremy),	33.8	18.6	3.5	— per cent.
„ (D. & H.),	33.79	18.35	—	1.09 „
Calculated,	33.68	18.37	7.63	1.12 „

Sulphammonate and *sulphamidate* are respectively nitrilo-sulphate and imidosulphate (Berglund).

