ON THE DECOMPOSITION OF SODIUM NITRATE BY SULPHURIC ACID, II.

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Received May 24, 1901.

ON a former occasion[1] I presented to this Society a report on my work under the same title. The previous work had reference mainly to the conditions under which nitric acid distilled from a mixture of sodium nitrate and sulphuric acid.

Professor Lunge, in the second edition of his handbook "Sulphuric Acid and Alkali,"[2] quotes from the above cited article; but the process of decomposition in the said work, is still represented as $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$. I now report results of further investigation of this process. In the first part of the report already referred to, I have called attention to the strength of the nitric acid, which distilled at certain fixed temperatures, and I concluded, from the boiling-points, the temperatures of the residues in the retort, and the quality of the acid obtained, that during the second period all nitric acid had distilled off, and that only a disulphate was left in the retort.

I have since gone over the work again, and considered not only the distilled acid, but also the residues in the retort, which remain after each period of distillation. For this reexamination I used, for each period of distillation, a fresh quantity of nitrate and sulphuric acid, interrupting each process after the distillation of acid had entirely ceased, at the temperatures given. For each test, 500 grams sodium nitrate and 550 grams sulphuric acid were used; the results obtained were in agreement with those already described, as far as the strength of nitric acid is concerned. I have, at several times, attempted to separate the liquid from the solid portions of the salt cake. It is quite easy to separate the liquid from undecomposed nitrate by pouring the hot mass off. This must be done when the mass is still quite hot, as on cooling it will readily crystallize.

The distillation of nitric acid below 100° was carried out by heating in a liter retort, 500 grams sodium nitrate and 550 grams sulphuric acid at a temperature of 130° in the oil-bath, and keeping as near that temperature as possible, for thirty-six hours.

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[1] This Journal, **13**, 246.

[2] Edition of 1893, p. 116.

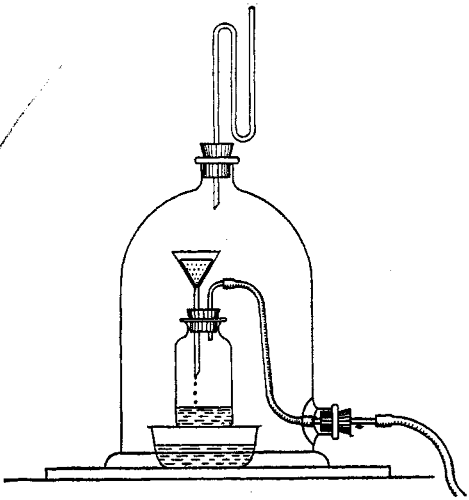
No further distillation could then be perceived. The residue in the retort consisted of unchanged nitrate and thick oily liquid. It was poured into a hot porcelain dish, which had been placed in an oil-bath of 100°, and from the hot mass a sufficient quantity of oily liquid was removed into another porcelain dish, where, on cooling, the liquid formed a crystalline salt in minute elongated prisms. The crystalline mass thus obtained, was left in a vacuum of 100 mm. at the ordinary temperature, for forty-eight hours, over sulphuric acid, and as it had lost nothing in weight, the sodium and sulphuric acid were determined, and gave the following results:

	Per cent.	Per cent.	Per cent.	Per cent.
Na	8.91	9.3	9.06	8.78
SO_4	90.0	90.9	87.75	85.1

which gives on the average for this salt:

	Per cent.
Na	9.01
SO_4	88.44

These results were obtained by the analysis of crystals furnished by solidifying the oily liquid above mentioned. As it is rather difficult to exclude the moisture of the air during the crystallization, and as thereby the crystals are destroyed, I have separated the solution from the solid residues in the retort, and then also from any possible excess of sulphuric acid, by filtration in vacuum, whereby the atmospheric air is almost totally excluded.



The simple apparatus is illustrated in the accompanying cut, and I may state here, also, that I arrived at the described construction of the apparatus after trying to obtain pure crystals by centrifugal filtration and vacuum filtration in a Gooch crucible; but I prefer at present, the following apparatus: the glass funnel contains a filter of platinum, finely perforated, and it can be seen that only the air in the bell-jar, which is dried over sulphuric acid, can come in contact with the substance on the platinum filter. Under a vacuum of 650 mm. the solution of salts in sulphuric acid is quickly removed from crystals remaining on the platinum, and any absorption of moisture is excluded. The average of three determinations gave

Na	9.476
SO_4	89.094

The sodium was determined as neutral sodium sulphate, and the sulphuric acid as barium sulphate. Comparing these with the composition of sodium trisulphate, $NaH_3(SO_4)_2$, we have the following:

	Calculated.	Found.
Na	10.550	9.362
SO_4	88.07	89.147
H_3	1.38	1.491
	100.000	100.000

The figures seem to be sufficiently close to the theoretical, to justify the conclusion, that during the first period of the action of sulphuric acid on sodium nitrate, the above indicated trisulphate is formed, provided that the temperature of the contents of the retort does not go above 100°. At this period then, the residue in the retort consists of the remaining sodium nitrate and sodium trisulphate. The process that has taken place, may therefore, be expressed by

$$NaNO_3 + 2H_2SO_4 = NaH_3(SO_4)_2 + HNO_3,$$

and if the temperature is not raised above 100°, no further action of sulphuric acid on sodium nitrate can be perceived.

The second period of acid distillation ends at a temperature of 121°. For the investigation of this period, 500 grams sodium nitrate and 550 grams sulphuric acid were distilled in the same manner as before, but the temperature, after the first period of about 100°, was raised in the oil-bath to 165° and kept so, until all trace of acid, distilling at 121°–122°, had disappeared from the residue.

This was again poured hot into the heated porcelain dish, parts of the liquid cooled to crystallization, crystals dried in a desiccator over calcined potash at about 100 mm. pressure and finally sodium and sulphuric acid determined.

The figures obtained in these determinations are rather irregular ; they gave as an average

	Per cent.
Na	18.730
SO_4	81.310

and compare with the acid sulphate of sodium thus :

	Calculated.	Found.
Na	19.166	18.730
SO_4	80.000	81.310
H	0.834	......
	100.000	100.040

It is probable, that at the end of this phase some of the trisulphate, $NaH_3(SO_4)_2$, was still left in the residue ; but it seems reasonable to assume the existence of $NaHSO_4$ in the salt cake, which now remains in the retorts.

The conclusions, which may safely be drawn from this work, are :

During the first period of action of sulphuric acid on sodium nitrate, polysulphate of the composition $NaH_3(SO_4)_2$ is formed, thus :

$$NaNO_3 + 2H_2SO_4 = NaH_3(SO_4)_2 + HNO_3.$$

The nitric acid, thus set free, is the true first hydrate and it distils over at its boiling-point between 81° and 88°.

The residue in the retort consists of trisulphate and nitrate, still undecomposed. On raising the temperature, the second phase of the process begins; the trisulphate acts at the higher temperature on the remaining nitrate

$$NaH_3(SO_4)_2 + NaNO_3 = (NaHSO_4)_2 + HNO_3,$$

and if this is carried out to the finish, the residue in the retort will consist entirely of $NaHSO_4$; and the acid distilling should also be HNO_3.

At the beginning of the distillation, free sulphuric acid is acting on a part only of the nitrate at a low temperature, at which the first hydrate distils undecomposed ; during the second period, the action of the trisulphate on the remaining sodium nitrate requires a higher temperature, at which nitric acid of the composition HNO_3 begins to decompose, and H_2O is always formed from HNO_3. The acid distilling during the period is, therefore, of a different concentration and is sometimes called the second hydrate. This investigation will be continued.

NEW YORK, December 20, 1900.