

ISMA* Technical Meetings

Cambridge, United Kingdom

15-17 September 1953

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

The Theory of the Kachkaroff Sulphuric Acid Process

by SVEN NORDENGREN*

THE processes for the production of sulphuric acid in lead chambers or towers have practically been developed without any exact knowledge of the chemical reactions leading to the formation of sulphuric acid. Up to about 1925 the theory of Lunge for the lead chamber process was generally believed. According to this theory, the sulphuric acid was formed in the gaseous phase of the lead chambers, a hypothetical compound, SO_2NH_2 , called 'sulphonitronic acid,' identified as the blue or purple acid sometimes seen as a colouring of the chamber acids, being regarded as the primarily formed compound from which sulphuric acid was derived.

In the middle of the twenties it was found that the main reactions, by which sulphuric acid was formed in the lead chambers, took place in the liquid phase; that the sulphur dioxide consequently had to be absorbed in the liquids present; that those liquids mainly consisted of sulphuric acid of varied concentrations containing nitrosylsulphuric acid in solution; that this nitrosylsulphuric acid, SO_2NH , was, according to temperature and concentration of the sulphuric acid, more or less hydrolysed into sulphuric acid and nitrous acid; that the nitrous acid in turn was partly decomposed into various nitrogen compounds staying in the solution; and finally that the reactions forming these compounds, nitrous acid included, were equilibrium reactions. From a paper by the author publishing the results of these investigations the following may be quoted:

'Nitrosylsulphuric acid will always be hydrolysed (to a certain extent) into sulphuric acid and nitrous acid; nitrous acid will be decomposed into N_2O_3 and water; N_2O_3 into NO and NO_2 ; the latter compound will form N_2O_4 , which oxide with strong sulphuric acid will form an equilibrium with nitrosylsulphuric acid and nitric acid. In this way all compounds mentioned will be present in a solution of nitrosylsulphuric acid in sulphuric acid, although, owing to the small grade of hydrolysis possible, only in very small quantities. All reactions being equi-

lium reactions, the bringing in of a reductive such as SO_2 will cause a disturbance of all these equilibrium reactions.'

This still left open the question of the main sulphuric acid-forming reaction. Other investigators made it clear that SO_2 in solution acted as H_2SO_3 . There would be a possibility of this compound reacting with HNO_2 itself or with N_2O_3 , NO_2 , N_2O_4 , or even with HNO_3 , small quantities of all these compounds being likely to be present in a partly hydrolysed solution of nitrosylsulphuric acid. No one suggested that the sulphurous acid would react with undecomposed nitrosylsulphuric acid, which would be contradictory to the fact that the oxidation process reaches its maximum when the nitrosulphuric acid is completely decomposed by hydrolysis.²

Further investigations showed the likeliness of nitrous acid itself being the main although not the only oxidiser. It had been known for a long time that if SO_2 was led into an aqueous solution of HNO_2 it was oxydised and the nitrogen compounds partly reduced to N_2O . It was now shown that H_2SO_3 might react with HNO_2 in two ways: either reducing the nitrogen compounds to NO or to N_2O . It all depends on whether there is a surplus of HNO_2 , or of H_2SO_3 .³

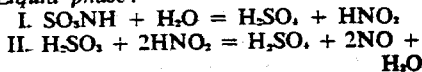
The reason given is the following. In the first part of the reaction a radical HNO , called 'nitroxyl,' is being formed:

- a/ $\text{H}_2\text{SO}_3 + \text{HNO}_2 = \text{H}_2\text{SO}_4 + \text{HNO}$;
With a surplus of nitrous acid NO is formed:
- b/ $\text{HNO} + \text{HNO}_2 = \text{H}_2\text{O} + 2\text{NO}$;
but with a surplus of H_2SO_3 , two 'nitroxyl' radicals will form N_2O :
- c/ $2\text{HNO} = \text{H}_2\text{O} + \text{N}_2\text{O}$;

At the concentrations of the Lead Chamber Process there is a surplus of HNO_2 in the solutions, and the reaction, at least normally, will proceed according to reaction b.

It is generally believed to-day that the main reactions of the Lead Chamber Process are as follows:

Liquid phase:



* Landskrona, Sweden.

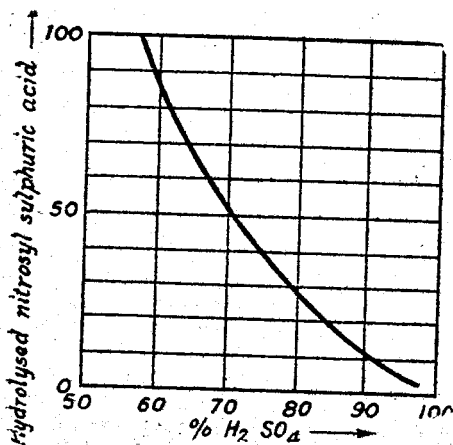
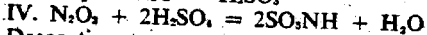
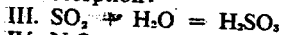


Fig. 1. Hydrolysis of 0.1 m nitrosyl-sulphuric acid solved in sulphuric acid of varying concentration

Liquid to gaseous phase:

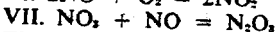
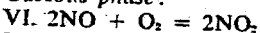
Absorption:



Desorption:

V. Desorption of NO

Gaseous phase:



The development of the Hugo Petersen tower units has greatly facilitated the understanding of the Lead Chamber Process.

The latest development in the manufacture of sulphuric acid with the aid of nitrogen compounds is the Kachkaroff Process. Its inventor, and later his followers, Guareschi in Italy and Salsas Serra in France, claim that the process itself is entirely new; that it is not a modification of the Lead Chamber Process as the Petersen process but that it is founded on facts hitherto unknown regarding the binding and unbinding of nitrogen compounds.

A new process for the making of sulphuric acid, founded on reactions yet unknown to science would be of the greatest interest not only to the sulphuric acid industry but also to science itself. Therefore, the theories and suppositions of the inventors should be put to test in the light of recent investigations and studies, with a view of finding out whether there is a probability of a new process, or if it is likely that the results obtained in the Kachkaroff plants can be explained

with the aid of our present knowledge.

At the technical meeting of the International Superphosphate Manufacturers' Association held in Paris during September, 1951, Mr. Salsas Serra presented an interesting paper on the development and evolution of the Kachkaroff process. The apparatus consists of one or two Glover towers, placed in series or parallel, three to five reaction towers and two Gay-Lussac towers. There is an outer and an inner circulation of acids. The cooled Glover acid goes to the last Gay-Lussac tower, from there to the first Gay-Lussac, and the nitrous sulphuric acid thus produced is de-nitrated on the first Glover tower. There is an inner circulation of nitrous sulphuric acid over the production towers which are partly packed with Raschig rings and have centrifugal atomisers to distribute the acid. The surplus of this acid is de-nitrated on the second Glover tower.

There is nothing specially new in these arrangements. A Kachkaroff plant will differ from a Petersen plant only in details or choice of materials.

The only difference of importance seems to be that the acids circulating over the production towers of a Kachkaroff plant are stronger than those of a Petersen plant, 61-64°Bé instead of 59-60°Bé. They have a nitrogen content corresponding to 5-10 per cent N_2O_3 , which is considerably more than in the Petersen plants.

High Content Understandable

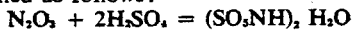
This high nitrogen content is quite understandable. Only the hydrolysed part of the nitrosylsulphuric acid is acted upon by the sulphurous acid according to formula I. Fig. 1 shows a diagram of the hydrolysis of 0.1 m. nitrosylsulphuric acid in sulphuric acid of varying concentration.* In order to obtain a constant quantity of 'free' nitrous acid, it will be necessary to increase the total nitrogen content with rising concentration of the sulphuric acid, as the hydrolysis decreasing with increased concentration.

Salsas Serra now claims that the formation of sulphuric acid at such high concentrations depends on a compound hitherto unknown which is said to have a pronounced oxidising power. This will enable a much higher production per tower volume than in other tower plants such as the Petersen plants.

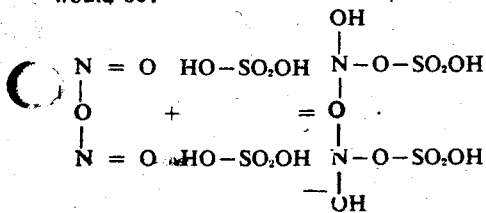
Calculated on the total tower volume, a Petersen unit will produce about 30 kilos of

100 per cent sulphuric acid per 1 cubic metre in 24 hours, with a very small loss of nitrogen, only 0.3 to 0.5 per cent 100 per cent HNO₃. According to Salsas Serra, a Kachkaroff plant would be able to produce about the double quantity with a loss of 1 per cent. As far as the author knows no proof has been given confirming this statement.

The compound which, hitherto unknown, is said to have an extreme oxidising power, is called by Salsas Serra 'hydrated nitrosulphuric acid' and supposed to be formed as follows:



Written in extended form the equation would be:



The existence of a compound with this composition is highly improbable. In the following the reasons of this opinion will be given.

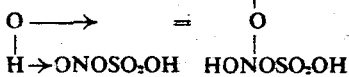
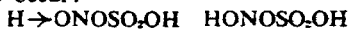
1. We know that the formula of the lead chamber crystals is SO₂NH. Solid crystals are formed when SO₂ reacts on concentrated nitric acid:



This compound should be regarded as ONO.SO₂.OH.

Insufficient Water

There is not enough water present in concentrated nitric acid to form (SO₂NH)₂.H₂O. We know that a solution of lead chamber crystals in sulphuric acid reacts exactly as nitrous sulphuric acid. It might perhaps be said that the compound (SO₂NH)₂.H₂O could be formed when lead chamber crystals are dissolved in sulphuric acid of certain density. This would necessitate a reaction between SO₂NH and water which is not very likely to occur:



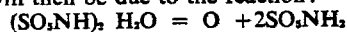
As far as the author knows there is no example of a water molecule being split up in this fashion, sending its three atoms in

different directions. What generally happens when water is added to a compound is that it is either added undivided as a hydrate or is split up in H + OH.

2. If a compound



has a special oxidising effect, it must be caused by the oxygen atom. The oxidation will then be due to the reaction:



We are then actually back to the hypothetical compound of Lunge called 'sulphonitronic acid,' the existence of which has never been proved.

3. If a compound (SO₂NH)₂.H₂O were formed, some signs ought to be found in the diagrams showing the speed of reaction between N₂O₃ and sulphuric acid of varying density. This reaction speed has been studied. The result is shown in Fig. 2, which also gives the reaction speed of NO₂(N₂O₄).

There is a strong resemblance between the reaction diagrams of N₂O₃ and of N₂O₄. Both fall to a minimum, from there to rise evenly with the increasing concentration of the sulphuric acid, although the minimum of the N₂O₃ reaction lies at about 18 per cent sulphuric acid and the minimum of the N₂O₄

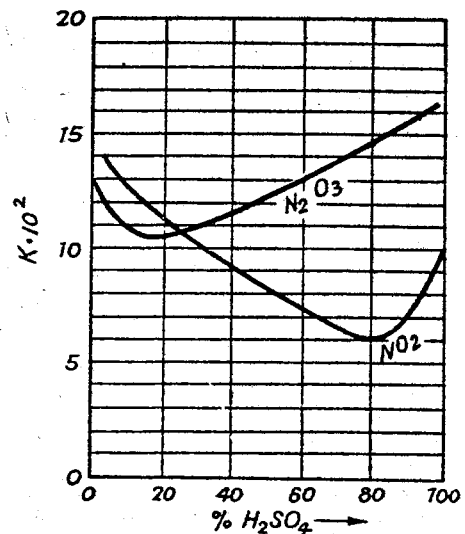


Fig. 2. Speed of absorption of N₂O₃ and NO₂ in sulphuric acid

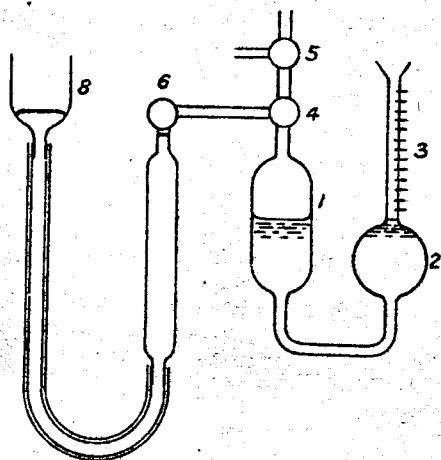
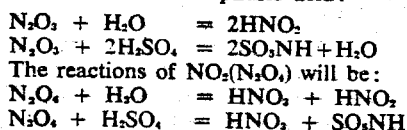


Fig. 3. Apparatus for the determination of relative reaction speed between SO_2 and nitrous sulphuric acid

reaction at about 82 per cent. In both cases the diagrams indicate that two reactions have taken place, the one undoubtedly with water and the other with sulphuric acid:



There is nothing in the diagram of N_2O_3 indicating that another reaction sets in at a concentration of about 80-86 per cent, which is the concentration of sulphuric acid used in the Kachkaroff plants.

There seems to be no doubt whatever that a compound $\text{SO}_3\text{NH}_2 \cdot \text{O} \cdot \text{SO}_3\text{NH}_2$ does not exist.

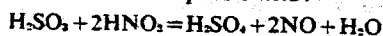
There would be a possibility that, at certain concentrations, water was added to the nitrosylsulphuric acid as a hydrate, $\text{SO}_3\text{NH}(\text{H}_2\text{O})$. It has, however, been found that no such hydrates are formed.

If the 'hydrated nitrosylsulphuric acid' does not exist, there would be no proofs of the existence of a special process forming sulphuric acid at concentrations between 61° and 64° Bé (80-86 per cent). It is, in fact, not very likely that sulphuric acid should be formed by two different processes, one above 61° Bé and the other at lower concentrations.

The increasing number of Kachkaroff plants being built in Italy and France necessi-

tates a definite answer to the question if there is a higher production in such plants per cubic metre although there seems to be no theoretical explanation to such a fact. In order to investigate this the author made the following tests.

A vessel (1-Fig. 3) was filled with nitrous sulphuric acid of various concentrations, the quantity of nitrosylsulphuric acid so determined always exactly the same quantity of 'free' HNO_2 was present. A quantity of SO_2 -gas was sucked into the vessel reacting with the nitrous sulphuric acid:



One volume of SO_2 transformed to sulphuric acid liberates two volumes of NO and the increased gas volume can be noted on the graduated glass tube marked 3. The small errors due to the solubility of SO_2 and NO in the acids are calculated not to influence the results.

The following nitrous sulphuric acids were used (parts by weight):

	I	II	III	IV
H_2SO_4	75	78	80	85
H_2O	25	22	20	15
'Free' HNO_2	1.6	1.6	1.6	1.6
Unhydrolysed SO_3NH	6.7	8.9	11.2	18.8

The results will be seen in Fig. 4. With a constant quantity of 'free' HNO_2 present

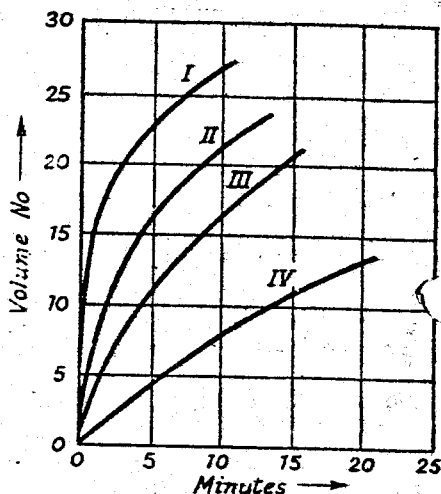


Fig. 4. Relative speed of reaction between SO_2 and nitrous sulphuric acid I-IV

the reaction will be slower with increased concentration of the sulphuric acid, which was to be expected as the solubility of SO₂ in sulphuric acid has its minimum at about 85 per cent H₂SO₄.

Nothing in these tests indicates a special process. There is only one process, the Lead Chamber Process, and Kachkaroff and Petersen plants both use this process. There may be small differences in the technical arrangements, in the cooling of acids and so on, by which certain differences in the production per cubic metre can be explained,

but fundamentally the Kachkaroff and Petersen tower 'processes' are identical.

REFERENCE

- ¹ Sven Nordengren, *Teknisk Tidskrift*, Stockholm, allm. avd., 1925, p. 189.
- ² Berl, Hillebrandt and Winnacker, *Z. anorg. u. allg. Chem.*, 214, 369 (1933).
- ³ E. Abel and Probst, *Sitz. ber. der Wiener Akad.* 145, 11 b 138 (1935) and 146, 11 b 201 (1937).
- ⁴ Diagram drawn by Stevinius-Nielsen after Hantzsch and Berger, *Z. anorg. u. allg. Chem.*, 190, 321 (1930).
- ⁵ Hantzsch and Berger, *Z. anorg. u. allg. Chem.*, 190, 321 (1930).
- ⁶ Szego, Molaguti and Lombardi, *Giorn. chim. ind. appl.* 14, p. 12, and 492 (1932) and 15, p. 189 (1933). Hantzsch and Berger, *loc. cit.*