CCCC.—*The Oxidation of Ammonium Sulphide.*

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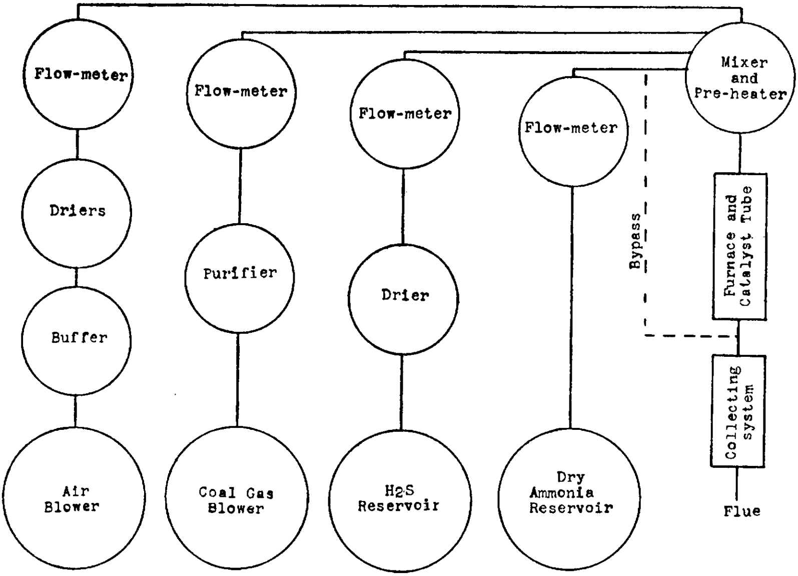
THE recovery of ammonia from coal-gas in the form of ammonium sulphate is usually effected by means of sulphuric acid, either by washing the crude gas directly with acid of suitable strength, or by first condensing the ammonia as a dilute liquor from which, after treatment with lime, the ammonia is distilled into the saturator.

It has often been pointed out that the crude gas contains more than sufficient sulphur to furnish the necessary sulphuric acid for the fixation of the ammonia, and several processes have been described by which ammonium sulphate may be obtained without the supply of extraneous sulphuric acid. The process of Cobb, depending on the precipitation of zinc sulphide and its subsequent reoxidation to zinc sulphate, and that of Feld, which is based upon a complex series of reactions involving the conversion of ammonium thiosulphate into tetrathionate and *vice versa*, with the subsequent formation of sulphate by decomposition of the tetrathionate (compare Meade, "Modern Gasworks Practice," 1916), have been shown to be commercially practicable. Both, however, are somewhat lacking in simplicity when compared with the usual processes of recovery in which sulphuric acid is used. A process simpler in theory is that of Burkheiser, in which sulphur is first removed by the iron oxide purifier charged with a specially active form of oxide, and then oxidised to sulphur dioxide by a blast of air. Two purifiers are used in an alternate manner, one being occupied in absorbing hydrogen sulphide from the gas while in the other the sulphur is being oxidised. The sulphur dioxide so obtained is finally united with the ammonia which has been separated at an earlier stage of the process, and the resulting ammonium sulphite

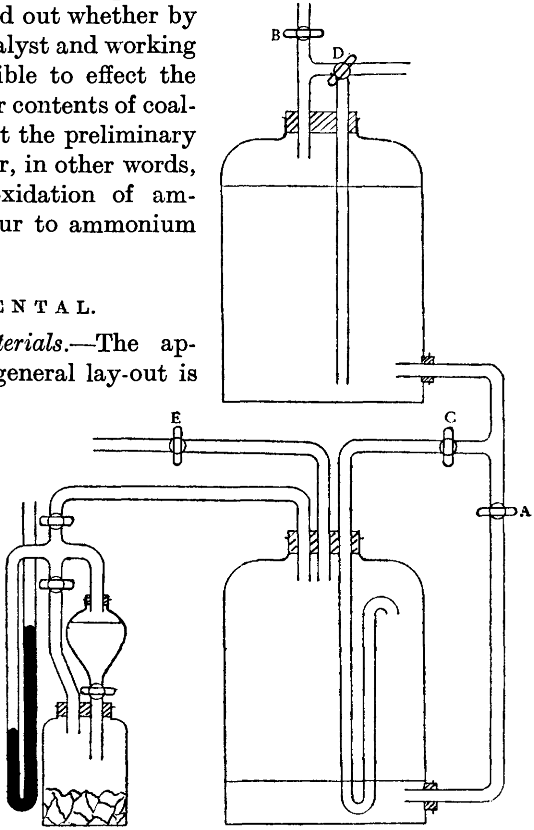
FIG. 1.



is oxidised in the dry state to sulphate by a current of warm air. The process may be represented by the equations:

(1) (First purifying tower), $Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$.
(2) (Second tower), $2Fe_2S_3 + 9O_2 = 2Fe_2O_3 + 6SO_2$.
(3) $2NH_3 + SO_2 + H_2O = (NH_4)_2SO_3$.
(4) $2(NH_4)_2SO_3 + O_2 = 2(NH_4)_2SO_4$.

FIG. 2.



The primary purpose of the present investigation was to find out whether by a suitable choice of catalyst and working conditions it was possible to effect the oxidation of the sulphur contents of coal-gas in one stage without the preliminary removal of ammonia, or, in other words, to effect the direct oxidation of ammonium sulphide vapour to ammonium sulphite or sulphate.

EXPERIMENTAL.

Apparatus and Materials.—The apparatus of which the general lay-out is represented in Fig. 1 consisted of:

(1) Apparatus for the preparation and storage of the gases employed.
(2) Flow-meters to measure the rate of supply of each gas.
(3) A mixer and pre-heater.
(4) The catalyst tube with its heating furnace.
(5) The collecting system for the solid products.

Air and coal-gas were introduced by means of blowers of the usual laboratory type operated by means of a small filter-pump, the inlet tube of the pump being open to the air in the first case and in the second connected to the gas tap. Ammonia obtained from a cylinder was conveniently stored in and delivered from a bottle of ammonium thiocyanate in the manner described by Foote and Brinkley (*J. Amer. Chem. Soc.*, 1921, **43**, 1178). Hydrogen sulphide was obtained in a pure condition by the action of water on aluminium sulphide, freshly prepared from its elements. The reaction was violent and the gas had therefore to be delivered from storage vessels. The apparatus used had some novel features represented in Fig. 2. It enabled several litres of gas to be stored over its saturated aqueous solution, the gas being brought in with taps A and B open and C, D, and E closed. By closing A and B and opening C and D the gas could then be delivered under a constant head through tap E. The taps on the generating bottle enabled the latter to be detached, recharged, filled with hydrogen sulphide and replaced without air being admitted to the storage vessels.

The gases, freed from moisture and dust, were delivered by fine-adjustment taps to flow-meters of the usual capillary type. The flow-meters for air and coal-gas were calibrated by measuring the outflow of gas for different readings of the instruments, those for ammonia and hydrogen sulphide by chemical absorption and weighing of the gas passing in a measured interval. It may be useful to note that the absorbent for hydrogen suphide was lime slaked with a strong solution of ferric chloride and made up into granules of convenient size. This absorbent is rapid and complete in its action and gives excellent quantitative results when backed by a soda-lime tube to absorb the water liberated. None of the flow-meters gave a linear relationship between pressure and rate of flow, but tests made at intervals during the experiments showed that the calibration figures remained satisfactorily constant when the gases were clean.

The mixer and pre-heater consisted of a wide glass spiral surrounded by hot water. This secured uniformity of composition and prevented the deposition of solid ammonium sulphides. From this apparatus the gas mixture passed by a short connexion into the catalyst which was packed in a silica tube of 16 mm. diameter heated in a resistance furnace. The furnace was wired in such a way as to secure uniformity of temperature, and the temperature of the catalyst was ascertained by a platinum–platinum-rhodium thermocouple. The temperature was maintained as constant as possible during a run by hand regulation, but it was recognised that in some experiments where a visible glow occurred in some parts of the catalyst the temperature recorded can only have been a mean. The thermocouple was so placed that it gave the temperature of the last parts of the catalyst to be traversed by the gas. The catalysts used filled the silica tube to a length of 25 cm.

Collection of the Products.—Although most of the ammonium sulphate obtained solidified as a vitreous mass in the silica tube within 10 cm. of the end of the furnace, the sulphite which the gases contained formed a very fine fume which was not absorbed by water in any form of bubbling apparatus or in a pumice tower 80 cm. long. Eventually it was found possible to collect the fume completely by means of an asbestos mat in a Buchner funnel fitted to the escape tube. In all experiments the fume so collected consisted of pure ammonium sulphite, as the following analyses show; no other sulphur product was detected in the fume:

NH_4 = 31·10, 30·95, 30·49%. Mean 30·85%.

$$\left.\begin{array}{l} SO_3 \text{ (by iodine)} = 68{\cdot}37,\ 69{\cdot}00,\ 68{\cdot}71\%. \\ \quad\text{(by } BaSO_4) = 68{\cdot}73,\ 69{\cdot}12,\ 69{\cdot}00\%. \end{array}\right\} \text{Mean } 68{\cdot}82\%.$$

Calc. for $(NH_4)_2SO_3$: NH_4, 31·03; SO_3, 68·97%.

The asbestos mat collector was inconvenient, since it produced an appreciable back-pressure. In view of the evidence obtained of the nature of the fume, it was therefore decided to collect only such portion of the products as would separate in a long, wide exit-tube and to assume that the sulphur not accounted for in this product had escaped as ammonium sulphite. The exit gases in each experiment where this assumption was made were proved to be free from hydrogen sulphide.

The product was scraped out of the collecting tube as completely as possible by means of a nickel spatula and transferred, after being thoroughly mixed, to a weighing bottle. The products were nearly always apparently dry, but in a few cases where they appeared to be moist they were dried in a partially evacuated desiccator.

Analysis.—The ions $NH_4^{\bullet}$, S_2O_3'', SO_3'', SO_4'', and $NH_2{\cdot}SO_2'$ all appeared at various times in the products, as also did elementary sulphur. In the few cases where the ion $NH_2{\cdot}SO_2'$ appeared (the product was coloured yellow by ammonium aminosulphonate and its decomposition products) analysis was not carried out, since it was clear that oxidation was incomplete. The ammonium content was determined by distillation into standard acid. The determination of sulphite, sulphate, and thiosulphate in the product presented great difficulties, and success was only achieved by using the following method suggested by Mr. J. J. Manley, whose advice and assistance we gratefully acknowledge. The method depends on the slow oxidation of sulphite in air and the extrapolation from the iodine titre–time curve to the iodine titres before oxidation began (sulphite plus thiosulphate) and after it was complete (thiosulphate alone). A measured volume of water free from carbon dioxide * is placed in a large conical flask fitted with inlet and outlet tubes and also with a tube by which a pipette can be introduced for the removal of samples. Air, freed from carbon dioxide and saturated with water vapour by passage through a similar flask, is passed through the water for 2 hours to saturate it with oxygen, a small glass capsule containing a weighed quantity of the solid sufficient to give a solution about 0·15*N* in reducing power is dropped in, the stopper replaced, and the current of air restarted. After a definite time from the addition of the solid the air current is stopped, a measured sample removed and at once run into a measured volume of *N*/10-iodine solution, the excess being determined by thiosulphate. For the first half-hour samples are withdrawn every 5 minutes and afterwards every half-hour until a constant titre is reached. A characteristic example is given in the following table :

Time (mins.).	Iodine (c.c.).	Time (mins.).	Iodine (c.c.).	Time (mins.).	Iodine (c.c.).	Time (mins.).	Iodine (c.c.).
5	19·65	30	16·25	150	9·0	270	6·65
10	18·8	60	13·6	180	8·0	300	6·45
15	18·2	90	11·5	210	7·35	330	6·5
20	17·8	120	9·7	240	6·8	360	6·4
25	16·95						

Extrapolated for zero time, 20·3 c.c.; for infinite time, 6·4 c.c.

This analytical method, although laborious, gave very satisfactory results. Total sulphur was determined by oxidation of the whole by bromine-water and subsequent precipitation as barium sulphate. Elementary sulphur when present was obtained by difference from two estimations of total sulphur as barium sulphate, the first performed on the solid product, the second on the solution in water from which the sulphur had been removed by filtration. It is noteworthy that under the analytical conditions elementary sulphur does not react appreciably with iodine or with sulphite. Specific experiments failed to detect any such action.

Catalysts.—The following catalysts were investigated :

(1) *Burnt pyrites.* This was a commercial specimen from Tharsis pyrites and had the composition : Fe_2O_3, 87·34%; Cu, 2·14% (of which 1·11% was soluble in water, presumably as $CuSO_4$); S, 4·15% (2·43% soluble in water).

(2) *Ferric oxide gel.* Prepared by precipitating a solution of

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* Precautions against the entry of carbon dioxide in the air-stream or during the removal of samples by the pipette are necessary owing to the reaction between thiosulphate and unpurified air. Mayr has recently stated that the decomposition is not due to carbon dioxide (*Z. anal. Chem.*, 1926, 68, 274). The deleterious impurity in air is, however, removed by reagents which absorb carbon dioxide.

ferric chloride by sodium hydroxide. Before use it was dark brown and transparent and showed the characteristic conchoidal fracture of a gel.

(3) *Alumina powder.* (4) *Soft alumina.* (5) *Alumina gel.* These were all prepared by precipitating a solution of aluminium sulphate with sodium carbonate. They differed only in hardness; the hard gel had a conchoidal fracture but was not transparent.

(6) *Bauxite.* The specimen used contained some iron.

(7) *Pumice.* The sample used contained little iron. It was ground to convenient size and freed from dust.

(8) *Chromic oxide.* Some of the pumice used for catalyst (7) was boiled for 20 minutes in a saturated solution of ammonium dichromate, dried, and ignited.

(9) *Chromic oxide gel.* Prepared by precipitating a solution of chromic chloride with sodium carbonate. The gel structure was well defined and was not destroyed at 500°.

Tabulation of Results.—Analytical data for the various products are given under three headings which require some explanation. The values under " Found " are the actual percentages of each constituent determined analytically without any adjustment. In most cases these do not add up to 100% because the products are somewhat hygroscopic and absorb water during the operations of detaching from the collecting tube and mixing. Under " Dry " are the percentages calculated on the assumption that the deficiency was due to water. The justice of the assumption was in several experiments verified by analysis before and after drying in a desiccator. From the total weight of product collected and the " Dry " percentages it was possible to calculate what percentage of the sulphur introduced as hydrogen sulphide had been recovered in the solid product. These figures are given under " Recovery " in the last column of the tables. From the figures of the " Dry " analysis and from the calculated quantities of $NH_4^{\bullet}$ and SO_3'' equivalent to the sulphur not recovered, figures are obtained which are reduced to percentages and tabulated as " Corrected " (for the justification of this procedure see " Collection of the Products " above).

Ferric oxide catalysts. Ferric oxide was known to catalyse not only the Claus reaction ($2H_2S + O_2 = 2H_2O + 2S$) and the oxidation of sulphur dioxide to trioxide, but also the oxidation of ammonia (Maxted, *J. Soc. Chem. Ind.*, 1917, **36**, 777). It was, however, thought possible that by suitable choice of temperature, oxidation of the sulphur content of the gas might be brought about without oxidation of ammonia. On passing a mixture supplying 450 c.c. of air, 50 c.c. of hydrogen sulphide, and 50 c.c. of ammonia per minute over the pyrites catalyst, some reaction occurred at as low a temperature as 150°, but at no temperature up to 400° was any considerable amount of solid deposited. At all temperatures the solid product was sulphur, formed by the Claus reaction, and the water formed was considerably more than corresponded with the sulphur. It was thus evident that ammonia also was being oxidised, the oxidation being apparently to nitrogen and water since no acidic nitrogen could be detected among the products. With ferric oxide in this form, therefore, ammonia was oxidised before a sufficient temperature was reached to carry the oxidation of hydrogen sulphide further than the Claus reaction.

With ferric oxide gel and an increased supply of air at 195° a small solid product collected, containing principally sulphur and ammonium aminosulphonate. A similar product was obtained at 200°, but it also contained sulphite and thiosulphate. At 235° a bright glow was observed in the front portion of the catalyst and the solid product was very small; much of the ammonia was oxidised. At 250°, there was no solid product and little fume; there was a bright glow and the ammonia was almost completely burnt. The products were again nitrogen and water.

From these experiments it appears that ferric oxide in any form is too active a catalyst in ammonia oxidation to permit its use for the desired reaction. In view of these results some experiments were performed with air and ammonia alone, mainly with a view to establish more certainly the products of oxidation. A very unexpected result was obtained, for it was found that pure ammonia was not oxidised at all on the ferric oxide catalyst between 200° and 300°, although in presence of hydrogen sulphide at these temperatures oxidation is extensive and vigorous. On adding a small quantity of hydrogen sulphide to the entering gas, oxidation began with a glow in the catalyst and continued after the supply of hydrogen sulphide was cut off. Hydrogen sulphide accordingly acts as a promoter for the oxidation of ammonia on ferric oxide gel. In none of these experiments was there any further oxidation of the nitrogen.

Alumina catalysts. Alumina in the form of bauxite is known to be an efficient catalyst for the Claus reaction and, so far as we have been able to discover, is not a catalyst for ammonia oxidation. The first catalyst used was alumina powder, to which the gases were supplied at the rate of 800 c.c. of air, 50 c.c. of hydrogen sulphide, and 100 c.c. of ammonia per minute. This catalyst had the desired properties : in a typical experiment at 230°, the product was white and dry, and completely soluble in water. There was no hydrogen sulphide or sulphur in the products. Analysis gave :

	Found.	Dry.	Corrected.	Recovery.
NH_4	25·60	30·58	30·95	23·9% S
SO_4	6·43	7·68	1·60	
SO_3	24·44	29·20	60·66	
S_2O_3	27·24	32·54	6·79	

The product was thus mainly ammonium sulphite, a large part of which was lost in the very copious fume. The somewhat high proportion of thiosulphate shows that at 230° oxidation had not been carried completely to the sulphite stage. The thiosulphate is formed from sulphur resulting from the Claus reaction.

The alumina powder, though efficient as a catalyst, was mechanically unsuitable, since it produced a considerable back-pressure. Further experiments were accordingly performed with the coarser materials, the gas supply being 650 c.c. of air, 50 c.c. of hydrogen sulphide, and 100 c.c. of ammonia per minute in all experiments afterwards undertaken. The experience gained with alumina powder had shown this to be the optimum mixture.

The following table summarises the experimental results with soft alumina and with alumina gel. Percentages of ammonium are omitted for reasons of space, although they were in each case determined. In most of the products of which analyses are given, the ammonia content corresponded within a few units per cent. with the total sulphur acids found, a slight deficiency in some experiments being traced to the presence of a small amount of ammonium metabisulphite in the product. This fact is in itself a proof that ammonia was not oxidised by this catalyst, since the ammonia supplied was only enough for complete reaction with the sulphur acids.

	Found.			Dry.			Corrected.			Recovery
Temp.	SO_4.	SO_3.	S_2O_3.	SO_4.	SO_3.	S_2O_3.	SO_4.	SO_3.	S_2O_3.	(% S).
				Soft alumina catalyst.						
222°	No appreciable product. Much sulphur deposited in catalyst.									
261	Much sulphur with moisture and aminosulphonate.									
338	3·90	66·60	—	—	—	—*	3·36	66·50	—	88·2
454	11·94	59·28	—	—	—	—	10·69	59·71	—	90·5
479	14·20	54·65	1·34	14·26	54·96	1·35	13·12	56·10	1·24	91·9
527	21·72	49·80	0·66	—	—	—	21·72	49·80	0·66	100
533	24·29	47·40	0·66	24·84	47·82	0·69	18·20	52·46	0·50	75·3
				Alumina gel catalyst.						
395	15·50	47·74	9·78	15·66	48·25	9·89	7·72	58·76	4·89	51·6
424	16·79	51·53	1·70	16·85	51·75	1·80	15·65	52·97	1·69	92·9†
506	17·30	54·40	—	—	—	—	17·30	54·40	—	101·0
550	4·65	65·50	—	4·69	65·76	—	3·72	66·48	—	79·8

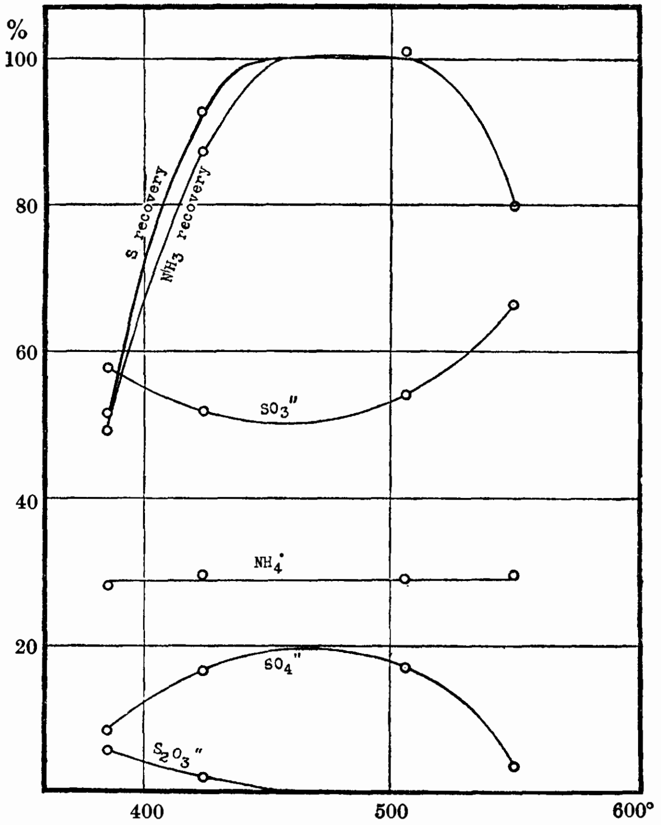
* Where no figures are given under " Dry " the original product contained only a negligible amount of water.

† This product also contained a little free sulphur which was produced during an accidental stoppage of the gas supply.

Fig. 3, which represents the results with alumina gel, shows clearly the effect of temperature on the behaviour of the catalyst. Only one catalyst diagram is reproduced here, but the diagrams of other efficient catalysts are quite similar in general aspect. The noteworthy features are the following :

(1) The percentage of sulphate in the product increases with temperature to a maximum and then falls off. This is due, first, to the increase in the velocity of the reaction $2SO_2 + O_2 = 2SO_3$ with temperature, and, secondly, to the exothermic character of the reaction.

FIG. 3.



Alumina gel catalyst ; air 650 *c.c. ;* H_2S 50 *c.c.;* NH_3 100 *c.c. per min.*

(2) The efficiency of the recovery increases as the proportion of the less volatile sulphate increases.

(3) The formation of thiosulphate appears to be a low-temperature effect due to the persistence of the Claus reaction.

The activity of ferric oxide in promoting the oxidation of ammonia was again shown in experiments in which we endeavoured to use the mineral bauxite as catalyst. The small percentage of iron contained in the mineral led to almost complete oxidation of the ammonia and no solid products could be collected.

Pumice catalyst. The following results showed that pumice also acted as an efficient catalyst for the oxidation of ammonium sulphide :

	Found.		Dry.		Corrected.		
Temp.	SO_4.	SO_3.	SO_4.	SO_3.	SO_4.	SO_3.	Recovery (% S).
426°	Yield very small.						
470	4·25	65·10	4·30	65·99	3·40	66·60	80·4
553	5·00	65·30	—	—	4·70	65·94	94·8
662	11·75	57·80	12·05	59·21	11·20	59·90	98·0
772	9·70	69·65	9·94	61·20	7·95	62·54	80·2

These results are quite similar to those with pure alumina; the maximum formation of sulphate, however, occurs at a much higher temperature, and the amount is smaller than with alumina, in accordance with the sign of the heat change in its formation.

The data obtained with alumina and with pumice are in accord with the work of Knietsch (*Ber.*, 1901, **34**, 4069) on the kinetics of the contact process, as was shown by a series of experiments in which the ammonia was omitted from the entering gases but added to the products emerging from the catalyst tube. This change of procedure produced no appreciable alteration in the results, proving not only that the ammonia is itself unoxidised by the catalyst, but also that it has no effect on the sulphur dioxide–trioxide equilibrium.

Chromic oxide catalysts. Preliminary experiments with chromic oxide from ammonium dichromate and with chromic oxide gel showed that both materials catalysed the oxidation of sulphur dioxide, the gel being the more effective. On subjecting ammonium sulphide vapour and air to the action of the gel catalyst, however, it was found that chromic oxide, like ferric oxide, was a very active catalyst for ammonia oxidation. Much water was formed, but no solid product. The effluent gases were strongly acid, but the acidity was due to sulphur acids, no nitric acid being detected.

Experiments in Presence of Excess of Coal-gas.—Having established the possibility of quantitatively oxidising ammonium sulphide vapour to sulphite and sulphate, an attempt was next made to apply the process to a mixture approximating in composition to coke-oven gas. For this purpose a gas stream consisting of 650 c.c. of air, 50 c.c. of hydrogen sulphide, 865 c.c. of coal-gas, and 100 c.c.

of ammonia per minute was passed over the alumina gel catalyst. With the dry mixture the following results were obtained :

	Found.		Dry.		Corrected.		
Temp.	SO_4.	SO_3.	SO_4.	SO_3.	SO_4.	SO_3.	Recovery (% S).
510°	16·20	57·50	16·25	57·65	2·20	67·40	13·6
634	15·36	54·70	15·15	54·95	10·41	59·44	66·7

Since the gas from coal distillation is wet, experiments were also performed with the same mixture saturated with water vapour by passing up a 50 cm. tower of wet pumice.

	Found.			Dry.			Corrected.			
Temp.	SO_4.	SO_3.	S_2O_3.	SO_4.	SO_3.	S_2O_3.	SO_4.	SO_3.	S_2O_3.	Recovery (% S).
484°	21·28	37·08	9·06	—	—	—	5·95	59·96	2·55	33·6*
641	16·00	54·10	—	16·23	54·97	—	12·39	58·27	—	76·1

* This product also contained 7·13% of free sulphur, or 2·01% corrected.

In all these experiments the coal-gas interfered seriously with the efficiency of the transformation. The products were smaller in amount and much contaminated with tar, especially at the lower temperatures. At the higher temperatures, a green liquid was found in the collecting system and the products had a strong garlic odour suggesting carbonyl sulphide. On standing, the green liquid deposited a white solid, too small in amount for identification.

It thus appears that, although the oxidation of ammonium sulphide in presence of coal-gas takes mainly the same course as with the pure gas, it does not run smoothly and gives rise to troublesome by-products.

Summary.

1. Ammonium sulphide vapour can be quantitatively transformed to a mixture of ammonium sulphite and sulphate by atmospheric oxidation at temperatures of 450° to 650° in presence of a suitable catalyst.
2. Alumina, best in the form of gel, is the most efficient catalyst for this reaction, but pumice can also be used.
3. Ferric oxide and chromic oxide actively catalyse the oxidation of ammonia, hydrogen sulphide acting as a promoter to ferric oxide.
4. Experimental devices described in this paper include an apparatus for generation, storage and delivery of pure hydrogen sulphide at constant pressure, a quantitative and rapid absorbent for hydrogen sulphide, and a method for the quantitative determination of sulphite and thiosulphate in mixtures of the two.

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