

A. ARROWSMITH

Department of Chemical Engineering
University of Birmingham
Birmingham, B15 2TT — U. K.

A. B. HEDLEY

Department of Chemical Engineering
University of Sheffield
Mappin Street
Sheffield S1 3JD — U. K.

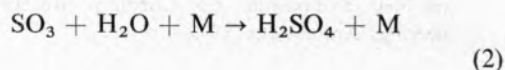
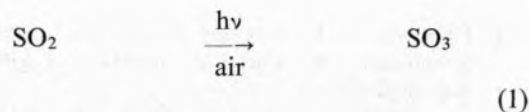


THE FORMATION OF AMMONIUM SULPHATE PARTICLES BY ATMOSPHERIC REACTIONS⁽¹⁾

The mechanism of formation of ammonium sulphate in the atmosphere is of fundamental importance for both determining its source and possible schemes for its control. Many results have been published concerning the oxidation of sulphur dioxide, which is produced in abundance during the combustion of fossil fuels. These have led to the prediction of reaction rates for photochemical oxidation, and the absorption of the gas in water droplets and aqueous phase oxidation. Comparison with observed atmospheric rates have shown considerable deviation. More recently, direct gas to particle conversion of mixtures of sulphur dioxide, ammonia and water vapour in air has been investigated.

1 — INTRODUCTION

Soluble atmospheric particulates give rise to reduced visibility and thermal radiation while airborne and may give rise to material damage and reduced soil fertility upon deposition through rain water wash out. As ammonium sulphate has been shown to account for 60 % or more of soluble atmospheric particulates in a number of places in the UK [1], the mechanism of its formation is of fundamental importance for both determining its source and also to suggest possible schemes for its control. The emission of sulphur dioxide from the combustion of most fossil fuels has led to many studies of possible routes for its oxidation to sulphate in the presence of ammonia or an ammonium ion. Aerosol formation by the photo-oxidation of sulphur dioxide in air has been the subject of a considerable number of studies. The results have suggested that sulphur trioxide is formed as an intermediary and then rapidly hydrated to molecular H_2SO_4



The presence of ammonia in the atmosphere then leads to the formation of ammonium sulphate. Aerosol formation was measured by Cox [2] in a gaseous mixture of sulphur dioxide, nitrogen, oxygen

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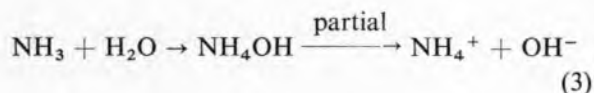
Whole set	500
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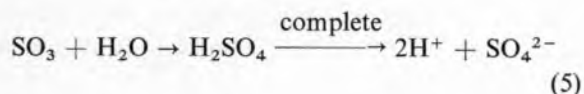
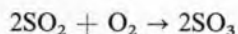
and water vapour as they flowed through an experimental chamber which was irradiated with light of wave-length 185-400 nm. Isotopic labelling of the sulphur and liquid scintillation counting were used for aerosol mass concentration measurements and a condensation nucleus counter was used to record particle diameters of 25-200 Å and concentrations of 10^2 - 10^6 particles cm^{-3} . These results indicated that the above mechanism may account for particulate formation in heavily polluted urban air, but that in rural air, with lower concentrations of sulphur dioxide, some other scheme such as condensation on existing nuclei is more probable.

It has been reported [3] that the rate of photo-oxidation of sulphur dioxide is increased by other atmospheric trace gases such as ammonia, olefins and nitrogen oxides. However, in the absence of ultra-violet radiation other schemes have to be found for sulphate formation.

Above poorly ventilated urban areas it has been postulated that sulphate is formed from the absorption of gaseous sulphur dioxide and ammonia in aqueous droplets followed by liquid phase oxidation. JUNGE and RYAN [4] measured the aqueous phase oxidation of sulphur dioxide bubbled through water by precipitating the sulphate. The concentrations measured were much lower than those observed in the atmosphere unless neutralising metal cations or ammonia were present in the aqueous phase. These results were later confirmed by VAN DEN HEUVEL and MASON [5] following measurements of the rate of ammonium sulphate formation in water drops exposed to air containing known concentrations of these gases. They suggested that as the rate of production of sulphate was two orders of magnitude higher in the presence of ammonia the reaction,



catalysed the aqueous phase oxidation



by releasing hydroxyl ions to neutralise the hydrogen ions.

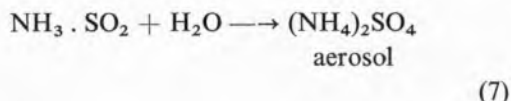
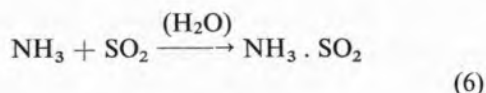
From a consideration of the equilibria involved in the above reactions SCOTT and HOBBS [6] and MCKAY [7] have predicted rates of sulphate formation which agree with the experimental measurements of VAN DEN HEUVEL and MASON [5], considering the limited accuracy of the experimental work. It has been reported that metal salts have a catalytic effect on the aqueous phase oxidation [8], but it is unrealistic to relate this to atmospheric reactions without prior identification of these salts at sufficient concentrations in atmospheric particulates. Although aqueous phase oxidation is a possible reaction route it does require the presence of droplets.

The results of laboratory experiments by SCOTT *et al.* [9] on the stratospheric reactions of anhydrous sulphur dioxide and ammonia, show the formation of solid products which varied in colour from white to yellow. This supports the observations of other workers who have investigated reactions between the two gases in the absence of free water surfaces. With an excess of ammonia a white 2:1 ($\text{NH}_3:\text{SO}_2$) product was formed which possessed a high heat of formation, 15 kcal mol^{-1} , suggesting a salt, whereas with an excess of sulphur dioxide a yellow (1:1) compound was formed with a low heat of formation, 1 kcal mol^{-1} , suggesting a relatively stable molecular cluster. The extrapolation of the vapour pressure above the 2:1 compound to -70°C gave a value of 10^{-5} Nm^{-2} . As this value corresponds to postulated partial pressures of ammonia and sulphur dioxide in the stratosphere, they suggest that this may provide the formation reaction for the aerosol layer. Although they did not measure reaction rates they observed that the reactions occurred rather violently, indicating the affinity of the anhydrous gases for each other. This may be further increased in the presence of water vapour.

SCARGILL [10], from an analysis of the products the interaction of ammonia, sulphur dioxide and water vapour at concentrations of 10-500 Nm^{-2} in air, has demonstrated the formation of ammonium sulphite with excess ammonia and ammonium pyrosulphite with excess sulphur dioxide. From a phase diagram for the equilibrium between these solids and the reactant gases, he concludes that at stratospheric temperatures the formation of ammonium sulphite would compete with the

anhydrous reaction suggested by SCOTT [9] and could be the primary product in the aerosol layer.

To support the experimental work on particle formation from gaseous reactions between sulphur dioxide, ammonia and water vapour in air, KIANG *et al.* [11] have presented a theory of heteromolecular nucleation. Based on the following reaction scheme,



they predict nucleation rates of $1 \text{ particle cm}^{-1}\text{s}^{-1}$ at 10 % relative humidity, for a partial pressure of $\text{NH}_3 \cdot \text{SO}_2$ of $4 \times 10^{-6} \text{ Nm}^{-2}$. At a relative humidity of 2 % a partial pressure of $6.6 \times 10^{-5} \text{ Nm}^{-2}$ would be required to produce the same nucleation rate, indicating the importance of relative humidity.

Thus, schemes suggested for the formation of atmospheric sulphate aerosols vary from gaseous phase reactions leading to particulate products, to absorption in droplets and aqueous phase oxidation. The extent to which these are important depends upon reactant concentration and temperature. As yet there has been little study of the effect of atmospheric aqueous aerosols on the rates of sulphate formation or experimental illustration of sulphate formation by way of heteromolecular nucleation under normal troposphere conditions.

2 — EXPERIMENTAL

The size and concentration of solid particles were measured as they were produced in the reaction between ammonia, sulphur dioxide and water vapour in air. The gases were mixed and passed through a horizontal glass column, 15 cm diameter, and 2 m long, fitted with four sampling points along its length. Flow visualisation studies ensured that mixing was rapid in the entry section of the reactor and iso-kinetic sampling ensured the removal of representative samples of the aerosol produced.

The effects of reactant adsorption on surfaces, and the limitations imposed on analytical techniques for determining low concentrations in such a difficult environment, were reduced by passing the ammonia and sulphur dioxide, at partial pressures of $0.12\text{--}0.6 \text{ kNm}^{-2}$ and water vapour at $0.68\text{--}2.48 \text{ kNm}^{-2}$ in air, through the column at room temperature. Provision was made for the injection of aqueous aerosols into the air stream at the reactor inlet. The droplet diameter in these aerosol clouds, which were produced by the ultrasonic nebulisation of deionized water, were in the micron size and concentrations were up to 1,000 droplets cm^{-3} . Particulate and aqueous aerosol size distributions were determined from samples drawn from the column which were then passed through the sensing head of a counter. A Royco 225 analyser picked up 90° light scattering patterns from the aerosol, analysed them and passed them to a sorter, counter and ten channel display unit covering the range $0.5\text{--}5 \mu\text{m}$.

3 — DISCUSSION OF RESULTS

A white crystalline cloud was formed immediately the reactant gases, at the partial pressures given above and in the absence of aqueous aerosol, were introduced and mixed in the glass column. A typical size distribution in a cloud, recorded by the particle counter, is given in fig. 1.

$$Y = \frac{\% \text{ of particles in the size range } (d_1 - d_2)}{d_1 - d_2}$$

$$x = \frac{(d_1 + d_2)}{2}$$

The particle sizes are approximately four times those reported by CARABINE *et al.* [12] from the mixing of sulphur dioxide and ammonia in nitrogen at similar concentrations. Their results, however, do not contain details of reaction times and, in the absence of water vapour it is possible that nucleation and crystal growth may be different. The variation in particulate formation with reactant concentration and relative humidity is shown in Table 1.

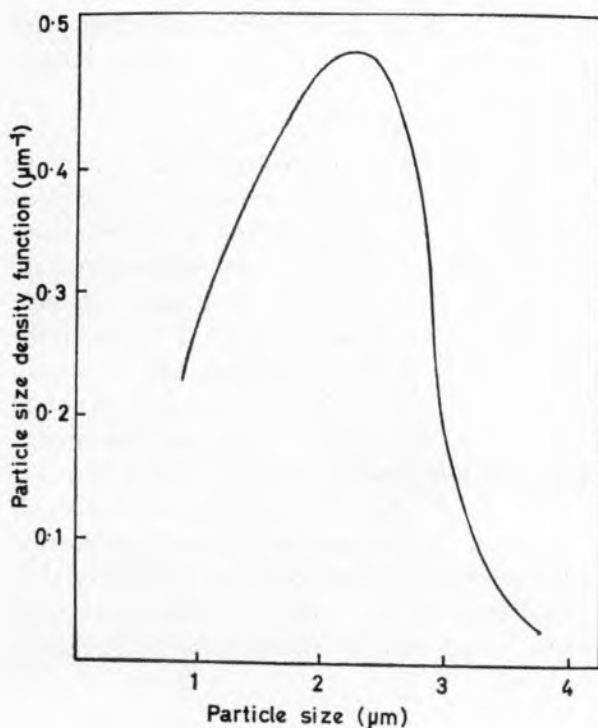


Fig. 1

Typical particle size density function curve

The flow rates of sulphur dioxide and ammonia through the column were in the range $0.8\text{--}7\text{ cm}^3\text{s}^{-1}$. For the last set of results in Table 1 a water aerosol, with a sauter mean drop diameter of $0.93\text{ }\mu\text{m}$ and a concentration of $10^2\text{ drops cm}^{-3}$ was injected into the air stream.

Observed cloud concentrations agree well with those reported by CARABINE *et al* [12] which suggests that water vapour and oxygen play a minor role in the nucleation process. The small increase in the cloud concentration in the presence of the water aerosol, which was of the same droplet size as the particulates, could be directly attributed to the water droplets. This further suggests that water has little effect, whether as a vapour or a free surface.

From the particle distribution measurements at the sampling point nearest to the gas inlet, and from the cross-sectional area of the column and the volumetric flowrate, estimates of the rate of particle formation are given in Table 1. These rates are in agreement with those reported by KIANG *et al.* [11, 13] for the heteromolecular nucleation of the sulphuric acid — water system at acid partial pressures of up to $1 \times 10^{-4}\text{ Nm}^{-2}$ at $25\text{ }^\circ\text{C}$, the nitric acid — water

system at acid partial pressures up to $1 \times 10^{-4}\text{ Nm}^{-2}$ at $20\text{ }^\circ\text{C}$ and the ammonia — sulphur dioxide — water system at partial pressures of postulated $\text{NH}_3\cdot\text{SO}_2$ of $1 \times 10^{-5}\text{ Nm}^{-2}$ at $25\text{ }^\circ\text{C}$. In contrast to the above table they predict an increase in nucleation rate of several orders of magnitude for a 10 % increase in relative humidity at relative humidities of 10 %, the effect decreasing at higher humidities. This difference may be a result of the large size of the measured particles, which have grown rapidly from the nucleation stage by such processes as adsorption and coagulation. These may not be influenced by the water vapour concentration to the extent that nucleation is.

The aerosol was sampled and filtered to determine the composition of the crystals and to provide further data on the mass flow and conversion of the reactants. Crystals deposited on the filter were dissolved in deionized water, sulphite was measured iodimetrically, sulphate gravimetrically after oxidation by peroxide and ammonium ion colourmetrically using Nelsslers reagent. The results of these tests were inconclusive and lead to uncertainty in the nature of the crystals.

The particles within the column were of a white crystalline form but a yellow solid was deposited at the sulphur dioxide inlet. This supports the observations of SCOTT *et al.* [9] namely the formation of a 2:1 ($\text{NH}_3\text{:SO}_2$) compound where the gas phase concentrations are comparable and a 1:1 compound

Table 1

Variation in particulate formation with reactant concentration

Number of particles cm^{-3}	Rate of particle $\text{s}^{-1}\text{ cm}^{-3}$	Relative humidity %	Reactant partial pressures kN m^{-2}	
			H_2O	SO_2 and NH_3
2,698	540	27	0.68	0.60
3,307	661	32	0.80	0.30
3,792	758	36	0.88	0.12
3,982	798	47	1.17	0.30
4,295	859	100	2.48	0.30
4,462	892	100 (1)	2.48	0.30

(1) Water aerosol injected into air flow.

where the sulphur dioxide concentration is considerably in excess. Figs. 2 and 3 show stereoscan photographs, of 2,000 times magnification, of the white crystals taken from the first and last sampling points. The difference in structural form of the two samples may be a consequence of the rate of growth of the crystals, the first being too fast to give the definite form of the latter, or the depletion of one of the reactants in the first section of the reactor. SCARGILL [10] from the studies of the infra-red spectra exhibited by white crystals formed from reactions between the gases at similar concentrations has identified ammonium sulphite when an

excess of ammonia was present, and ammonium pyrosulphite in the presence of excess sulphur dioxide.

An X-ray powder diffraction pattern from the crystals, collected at the sampling point nearest to the exit of the reactor, is shown in Fig. 4. Measured d-spacings of 4.27, 3.08, 3.0 and 5.16 and intensities of 100, 80, 80 and 20 at these spacings indicate that the crystals are ammonium sulphate. Although there was a time delay of several days before the analysis of the crystals, they were kept in a dark container. If oxidation had therefore occurred within the packed solid in such a time the atmospheric reaction, involving finely divided particles, would have occurred significantly faster and would consequently be of importance. However, because of the uncertainty of the composition of the crystals formed from the gas phase reactions it would be unwise to attempt to ascribe rates of formation to them.

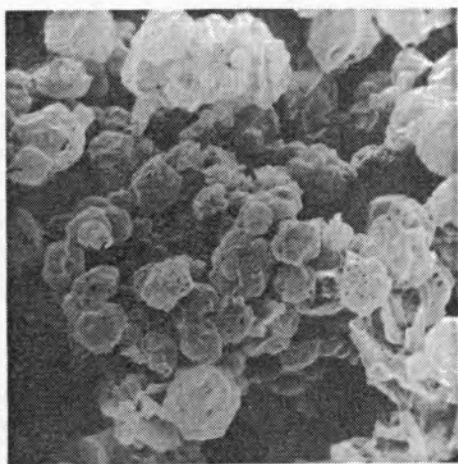


Fig. 2
Crystal formation at first sampling point

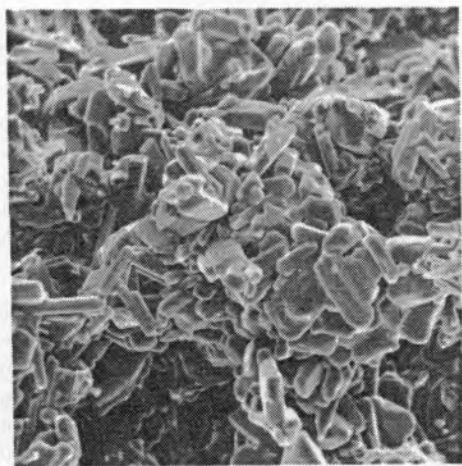


Fig. 3
Crystal formation at fourth sampling point

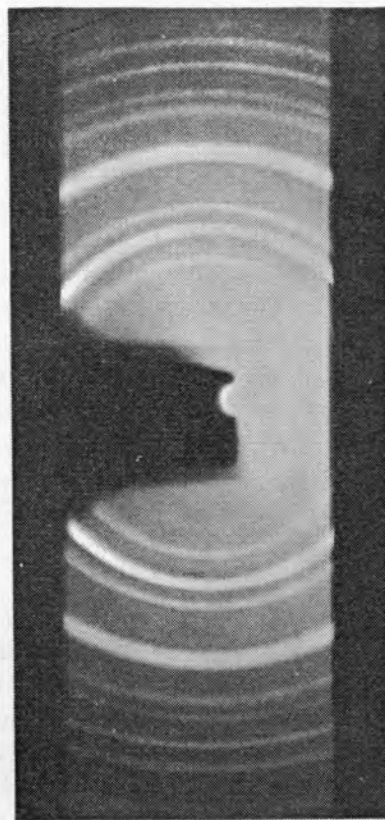


Fig. 4
X-ray powder diffraction pattern

4 — CONCLUSIONS

Although there is an agreement between the rates of particle formation predicted by heteromolecular nucleation theory and these experimentally observed rates, the concentrations considered in the two studies are considerably different, and should not therefore be compared directly. The experimental results show, however the importance of gas phase reactions between ammonia and sulphur dioxide leading to particle formation in atmospheric chemistry, by comparison with the aqueous phase reactions previously considered, and the rate-determining role played by the water concentration in such conversions.

This study also indicates that at the concentrations of sulphur dioxide, 0.2 kNm^{-2} , and water vapour, 9 kNm^{-2} , encountered in flue gases the addition of ammonia would result in aerosol formation which would facilitate removal of the acid gas.

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RESUMO

O conhecimento do mecanismo de formação de sulfato de amônio na atmosfera é de importância fundamental para a determinação da sua origem e dos esquemas de controle. Muitos resultados têm sido publicados sobre a oxidação do dióxido de enxofre, produzido em abundância durante a combustão de combustíveis fósseis. Com base nestes resultados fizeram-se previsões de velocidades de reacção de oxidação fotoquímica, de adsorção do gás em gotículas de água e de oxidação em fase aquosa. Comparando estes resultados com velocidades atmosféricas observadas experimentalmente, notam-se consideráveis desvios. Mais recentemente, tem sido investigada a conversão directa de gás a partícula de misturas de dióxido de enxofre, amónia e vapor de água em ar.