CONTENTS

SULFUR
IN
AUSTRALIA

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ATMOSPHERE: THE FORMATION OF SULFATE PARTICLES

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Introduction

The reactions of sulfur components in the atmosphere are basically the reactions of SO_2 since the other gaseous species, H_2S, is quickly oxidized to SO_2. The reactions of SO_2 in the atmosphere are numerous, especially when one considers reactions with atmospheric ammonia (Esmen and Ferguson, 1977). Of these reactions the oxidation and hydration reactions are by far the most important. The final product is sulfuric acid or sulfate particles since sulfuric acid is so reactive that it is removed nearly as quickly as it is formed. The reactions can occur in either the gaseous phase or in a condensed phase (in a liquid droplet or on a solid surface).

In the gas phase SO_2 is not readily oxidized and, without free radicals such as OH, HO_2 or peroxides, ozone, or atomic oxygen, its oxidation rate is insignificant. In turn, the majority of these species are only formed in special conditions when the intensity of solar radiation is high. Even in the best conditions, however, the reaction rate may be only about 0.1% per hour.

This reaction rate is too slow generally to account for the short lifetimes of SO_2 in the lower layers of the atmosphere. The heterogeneous reactions in water droplets or on the surfaces of particles are generally the largest masswise consumers of gaseous S. In water droplets the reaction may consume more than 10% of the SO_2 in an hour if the pH is greater than 6. The presence of trace amounts of metallic catalysts (including iron) can increase the reaction rate to the point where nearly all the SO_2 gas is consumed within the lifetime of a cloud (10 - 20 minutes).

The mechanism for masswise consumption of SO_2 and formation of sulfate seems somewhat clear. It is the continued presence of large numbers of sulfate particles that is unexplained. None of the reactions that appear effective in the formation of sulfate mass produce or nucleate new particles. Indeed, excess vapours are expected to condense out onto existing particles, increasing their mass, and not nucleate new particles. Yet, sulfate particles in the form of $(NH_4)_2SO_4$ are the most common constituent of the atmospheric aerosol, in terms of numbers of particles as well as in terms of the mass of particulates.
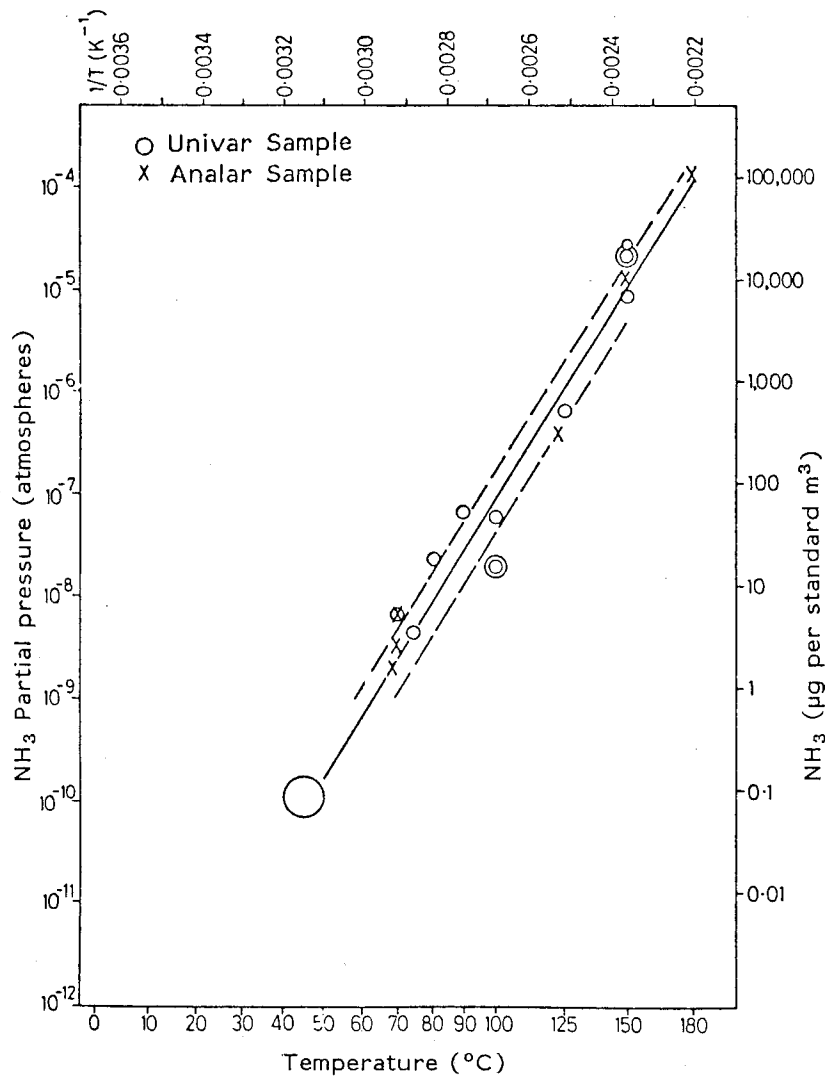

FIGURE 1   Measured ammonia partial pressures over ammonium sulfate samples

46

The present work is an attempt to explain how new particles are nucleated. To this end, the volatility of $(NH_4)_2SO_4$ was measured in terms of the equilibrium ammonia vapour pressures above the solid samples. The results are in accord with a simple theoretical model which suggests how the nucleation occurs.

Measurements

The vapour pressures were measured using a ring oven technique developed by Cattell and du Cros (1976) using a flow system (See Scott and Cattell, 1978). The measured vapour pressures are presented in Fig 1. The results were corroborated by a mass balance and a gas titration procedure at the higher temperature (150 and 180°C).

Interpretation

The general behaviour of the measured values of ammonia vapour pressure revealed that the results were adequately described by a simple model in which the vapour pressure depends directly upon the relative equivalents of acid in the solid. Effectively, the solid consists of $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4. Fig 2 presents some of the theoretical results as a function of the formula fraction NH_4HSO_4 in the solid. To understand this plot, consider the lowest line, the upward sloping, dashed line (marked H_2SO_4). At low values of the abscissa, the solid is nearly pure H_2SO_4, with the partial pressure of NH_3 below 10^{-40} atmospheres. As NH_3 is added to this mixture, we move along the abscissa, forming NH_4HSO_4, until a solid solution of 99% NH_4HSO_4 is obtained. At this point $(NH_4)_2SO_4$ starts to form, at the expense of the NH_4HSO_4; then we move up the solid diagonal line (marked $(NH_4)_2SO_4$) with diminishing values of the abscissa, until we have a NH_4HSO_4 solid concentration of about 10^{-6} and a vapour pressure of 10^{-25} atmospheres. Of course, here we are dealing with an environmental temperature of -100°C and normally at +25°C the value of the partial pressure of NH_3 would be about 10^{-9} atmospheres.

Particle Nucleation

Nucleation of new particles is possible in this system when one considers that the driving force for nucleation is the effective supersaturation $\bar{S}$ (Kiang et al, 1975):

$$\bar{S} = S_1{}^{x_1} S_2{}^{x_2} S_3{}^{x_3} \ldots S_n{}^{x_n} \tag{1}$$

where the S_n refer to the supersaturation of species n in the vapour and the x_n refer to the corresponding mole fractions in the solid. There are only two species in this system, NH_3 and H_2SO_4, so only the first two terms appear.

If we consider nucleation of pure NH_4HSO_4

$$\bar{S}_{NH_4HSO_4} = S_{NH_3}^{1/2} \cdot S_{H_2SO_4}^{1/2} \qquad (2)$$

If we consider nucleation of pure $(NH_4)_2SO_4$:

$$\bar{S}_{(NH_4)_2SO_4} = S_{NH_3}^{2/3} \cdot S_{H_2SO_4}^{1/2} \qquad (3)$$

Substituting in theoretical values for the equilibrium vapour pressures, it can be shown that

$$\bar{S}_{NH_4HSO_4} = (\text{Const.}) (P'_{NH_3} \cdot P'_{H_2SO_4})^{1/2} \qquad (4)$$

and

$$\bar{S}_{(NH_4)_2SO_4} = (\text{Const.}) (P'_{NH_3})^{2/3} \cdot (P'_{H_2SO_4})^{1/3} \qquad (5)$$

or

$$\frac{\bar{S}_{NH_4HSO_4}}{\bar{S}_{(NH_4)_2SO_4}} = (\text{Const.}) \left[\frac{P'_{H_2SO_4}}{P'_{NH_3}} \right]^{1/6} \qquad (6)$$

where the constants are all different combinations of equilibrium constants and the primed pressures correspond to ambient partial pressures.

If one substitutes in the appropriate equilibrium constants, equation 6 reveals that there is a greater tendency for the formation of acid sulfate particles at the lower temperature of the stratosphere than there is at the earth's surface. Surprisingly, there is little effect of partial pressure on this tendency because of the $1/6$ power.

The present results are most easily understood in terms of the equilibrium partial pressures of NH_3 and H_2SO_4, shown on Fig. 3. Here, as one expects, the H_2SO_4 partial pressure is quenched by the NH_3 partial pressure so that, roughly speaking, the product of the ammonia partial pressure squared with the sulfuric acid partial pressure remains constant. Note that, if any sulfuric acid is present

or acid particles are present, one expects the NH_3 concentration to be negligibly small. Since NH_4HSO_4 is often found in samples, NH_3 concentrations must be highly variable and certainly sensitive indications of atmospheric acid pollution.

With these general tendencies in mind, it is not hard to explain how homogeneous nucleation of ammonium sulfates
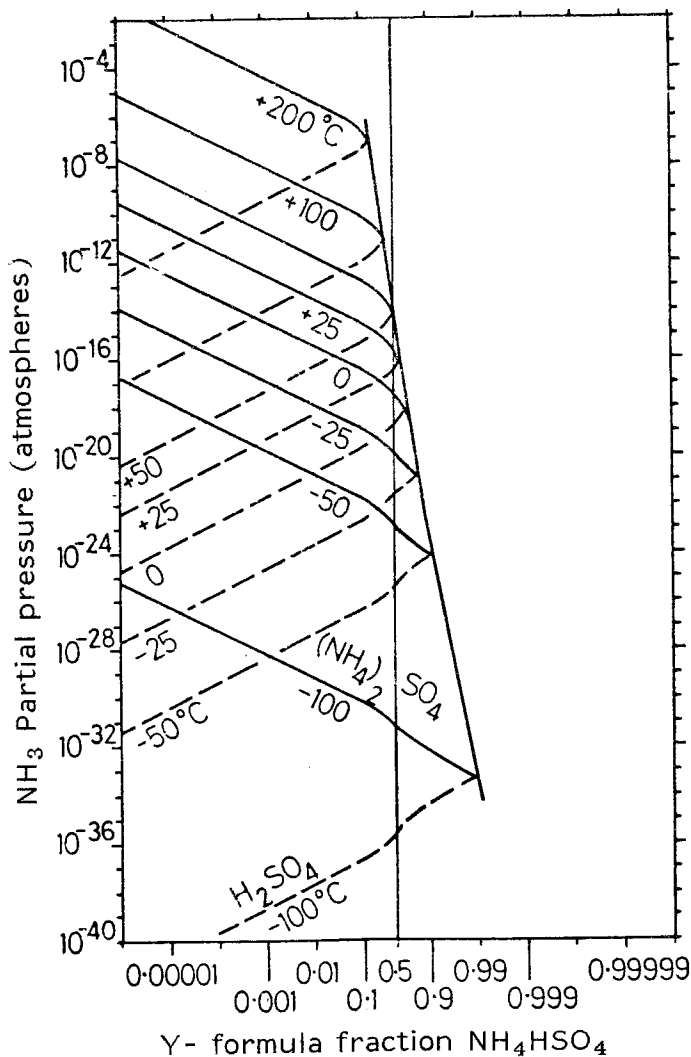

FIGURE 2   Computed ammonia partial pressure over solids of ammonium sulfate with ammonium hydrogen sulfate formula fraction Y

49

occurs in the atmosphere. Firstly, we must realize that the saturation ratios (Equations 1-3) are not the driving forces for condensation on existing particles. The driving forces for condensation are strictly partial pressures. Secondly, we must consider that, in the atmosphere, air from assorted sources is continually undergoing turbulent mixing. These different air parcels are likely to have quite different concentrations of ammonia and sulfuric acid, especially since both components are fleeting and the H_2SO_4 is produced from SO_2 in periods of intense solar radiation when trace components such as atomic oxygen, O_3, HO_2, or OH are present. To visualize the effect, consider the points P and Q on Fig. 3, which are under
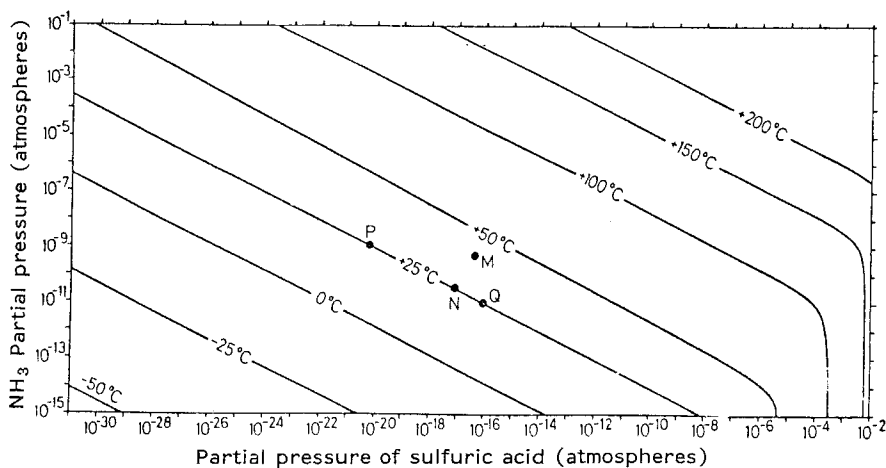

FIGURE 3   Expected equilibrium relationship between the partial pressures of gaseous sulfuric acid and gaseous ammonia

equilibrium conditions in different air parcels. The ammonia partial pressure at P is two orders of magnitude greater than at Q whereas the sulfuric acid vapour pressure at Q is four orders of magnitude greater than at P. If the two parcels come together, ammonia is expected to be transported in the opposite direction to the sulfuric acid and, when the two parcels are well mixed one expects the final concentrations of the mixed parcel to be represented by point M. This point has an effective saturation product with respect to equilibrium point N of 11. If homogeneous nucleation in such cases occurs with a saturation product of 1.5 (Landreth et al., 1975) surely such spacial homogeneities can nucleate new particles. In effect the atmosphere acts as a large chemical diffusion chamber.

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Discussion

Q.   I Galbally. Do you intend making measurements of the ammonia vapour pressure down to lower temperatures in the near future?

A.   The technique is hopeless at low temperatures because large background values, absorption, etc. are too overwhelming. Nevertheless, the theory fits well enough so that we have some confidence in the equilibrium values at low temperatures. Note that, if an estimate of the ammonia vapour pressures is available, one can get an estimate of the equilibrium values of sulfuric acid vapour pressures that exist in the atmosphere from the theory.

Q.   R Swaby. Could you tell me the prime source of the ammonia in this ammonium sulfate? Is it volcanic, from the burning of coal, or of biological origin?

A.   The most likely origin of it is animal waste, especially over Australia. We have made measurements of the pH of cloud water both upwind and downwind of Sydney, and the pH is generally higher than the CO_2 equilibrium point. This is very extraordinary because throughout the world you find acid rains and acid

clouds whereas in Australia we have excess ammonia. Thus we expect a different natural cycle of sulfur over Australia because of the presence of basic ammonia.

Q. R Manuell. In the stratosphere there are mainly sulfuric acid particles. What is the difference between the stratosphere and the lower stratosphere in this respect? Is there a different distribution of ammonia in the stratosphere?

A. Ammonia normally doesn't penetrate very far into the atmosphere. It is readily absorbed on surfaces, by water, rain, and SO_2 and doesn't get to the stratosphere, except on rare occasions. I think John Gras would say he has detected these intrusions of ammonia on occasions, though normally the stratosphere is acid. If you look at the equations I presented and put in the numbers, you find there is a better chance at lower temperatures for production of acid particles. That is, acid particles are most easily nucleated at the lower temperatures that exist in the stratosphere.

Q. G Ayers. I want to make a comment on that last question. John Gras can tell you that the residence time in the stratosphere is very long for the particles because the interchange of air with the troposphere is slow. In attempts to measure ammonia concentrations over the Australian continent in background air in clean conditions we obtain values around 1½ parts per billion. Similar values were found above the first inversion in the atmosphere. Yet, I suspect that the ammonia just doesn't get up to the stratosphere because the source is at ground level and the material must penentrate 10 or 12 km, generally through clouds. Volcanoes contribute negligible amounts of ammonia; they emit mainly acid materials such as SO_2 and sulfuric acid. The ammonia comes primarily from animal waste. In Europe with high animal density one measures something like 20-30 parts per billion of ammonia near the ground whereas we measure 1½ parts per billion at ground level south of Mt. Isa.