

The Formation of Sulfates and the Enhancement of Cloud Condensation Nuclei in Clouds¹

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ABSTRACT

The production of ammonium sulfate by oxidation of dissolved sulfur dioxide in cloud droplets in a wave cloud situation, and the resulting enhancement of cloud condensation nuclei (CCN) released from the cloud on evaporation, have been calculated. The condensational growth of droplets formed on 75 initial CCN sizes is considered simultaneously with the production of sulfates via the Scott-Hobbs mechanism in the droplets in an air parcel moving through a wave cloud. The results show that significant increases in the concentrations of CCN active at 0.5% supersaturation can be produced by SO₂ oxidation in wave clouds with short "flow-through" times (4 min) and with concentrations of SO₂ and NH₃ typical of unpolluted air (1 and 3 ppb, respectively). The sulfate production is found to decrease as the SO₂ concentration rises above 10 ppb. This effect is due to the limited buffering capacity of the NH₃.

The results of the calculations indicate that the in-cloud production of ammonium sulfate can probably explain previous observations of higher than ambient CCN concentrations in air from evaporating clouds, and that the rate of production of ammonium sulfate in clouds is sufficiently fast that it is probably the major worldwide source of these particles.

1. Introduction

It has been known for some time that in areas close to industrial activities sulfate particles comprise the major portions of the large ($0.1 \leq r \leq 1 \mu\text{m}$) aerosol particles (Junge, 1953, 1954, 1957). However, more recent measurements have shown that sulfate particles are also present in regions of the troposphere remote from human habitation. For example, Fenn *et al.* (1963) found that about 40% of the mass of aerosol particles in the air above the Greenland ice cap consisted of sulfate particles and Cadle *et al.* (1968) reported that more than 50% of the particles collected in five air samples near the ground in the Antarctic were sulfates. Even in the upper regions of the tropical troposphere sulfate particles dominate (Cadle *et al.*, 1970). Since the sulfates are normally found in conjunction with ammonia it is generally supposed that they exist as ammonium sulfate, although in some cases sulfuric acid has been suspected.

The primary source of atmospheric sulfates is the photochemical oxidation of SO₂ to SO₃ which rapidly attaches water and ammonia, but the rate of this oxidation is slow. Direct gas-to-particle conversion has received considerable attention particularly with respect to the stratosphere. However, in the lower troposphere the most likely source of sulfates is through the oxidation of dissolved SO₂ in cloud droplets.

There is a growing body of evidence that in addition to clouds acting as sinks for particles in the air [by

virtue of the particles serving as cloud condensation nuclei (CCN) or being collected by cloud particles] they also provide a medium for the growth of certain chemicals which may be released as particles when the clouds evaporate. Thus, Radke and Hobbs (1969), Saxena *et al.* (1970), Dinger *et al.* (1970) and Radke (1970) observed that CCN concentrations active at a given supersaturation are often higher in air from evaporating clouds than in the ambient air. Radke (1970) described measurements in which the concentrations of CCN (active at 0.5% supersaturation) were measured in air entering and leaving wave clouds over Mt. Rainier, Washington. In the three case studies presented by Radke, CCN concentrations in the air leaving the wave clouds were observed to be significantly higher than in the air entering the clouds.

Radke and Hobbs (1969) and Hobbs (1971) suggested that the enhancement of the activity of CCN in clouds might be due to the formation of sulfates in the cloud droplets through the conversion of SO₂ to SO₄²⁻ in the presence of trace amounts of NH₃ dissolved in liquid water. This reaction has been investigated in the laboratory by Junge and Ryan (1958) and Van den Heuvel and Mason (1963) and it has been discussed theoretically by Scott and Hobbs (1967) and McKay (1971). Georgii (1970) concluded that the so-called Scott-Hobbs mechanism could explain the main features of his airborne measurements of SO₂ and sulfate aerosols.

The purpose of the present paper is to determine whether the oxidation of dissolved SO₂ to produce sulfates in cloud droplets can significantly modify CCN

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distributions when operating on droplet sizes and time scales characteristic of wave clouds. The relative simplicity of wave clouds permits us to treat the chemistry in detail while still relationing a realistic cloud model.

2. Description of the model

In the model used in this paper a parcel of air is followed as it moves along a streamline through a wave cloud. As the parcel enters the cloud, droplets form on existing CCN. These droplets grow and evaporate as the parcel rises and descends. Simultaneously, SO_2 and NH_3 dissolve in the droplets, and the dissolved SO_2 is oxidized to sulfate ions. When the air parcel leaves the wave cloud and the droplets evaporate, each CCN upon which a droplet had formed has associated with it some additional mass of ammonium sulfate, produced during the transit of the cloud. The amount of this ammonium sulfate and the corresponding enhancement of the activity of the CCN is predicted by the model calculations. A more detailed description of the model follows.

a. The cloud model

The wave cloud model used for the calculations is a kinematic parcel model. A single parcel of air is considered as it follows a specified path through the atmosphere (see Fig. 1). The lee-wave phenomenon has received extensive theoretical attention in two-dimensional perturbation theory (e.g., Vergeiner, 1971). The streamlines are, to a first approximation, sinusoidal and this streamline shape has been adopted in this study. Specifically, we take

$$z(t) = z(0) + h[\cos(\omega t + \phi) - \cos\phi], \quad (1)$$

where z is the height of the parcel, t is time, and h , ω and ϕ define the sinusoidal streamline.

The results of the calculations are sensitive to three parameters which characterize a streamline in a wave cloud, namely, the vertical velocity of the air at the inflow edge of the cloud, the maximum vertical displacement of the air parcel, and the period of time that the air parcel remains above the condensation level. Only activated CCN can significantly increase in mass while in cloud droplets, and the mass of sulfate produced in the drop depends on the lifetime and the time-average size of the droplet. The vertical velocity at the inflow edge of the cloud (i.e., at the condensation level) essentially determines how many CCN are activated to form cloud droplets. The maximum vertical displacement of the air parcel determines the maximum liquid water content which, together with the number of droplets, determines the maximum droplet size. Finally, the time during which sulfates are produced is determined by the time that an air parcel remains above its condensation level.

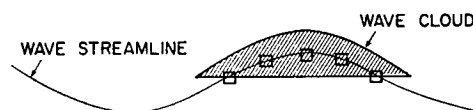


FIG. 1. Schematic diagram of cloud model. The squares indicate the successive locations of the cloud parcel followed in the computations.

The results of the chemical calculations are relatively insensitive to other details of the motion. The motion is assumed to be smooth, and interactions of the parcel with adjacent parcels—through exchange of heat, water vapor, liquid water, etc.—are not considered. Since lee waves occur under stable conditions where turbulence is suppressed, these approximations should not be too gross. Finally, the parcel is assumed to be at hydrostatic equilibrium with the undisturbed atmosphere. Large-amplitude lee waves are known to depart significantly from hydrostatic equilibrium but the departure is more important to the dynamics than to the thermodynamics of the wave.

With the above assumptions, the equations describing the evolution of the parcel can be written as

$$p(t) = p_e[z(t)], \quad (2)$$

$$(c_p + q_v c_{pw}) \frac{dT}{dt} = -gw - L_c \frac{dq_v}{dt}, \quad (3)$$

$$\frac{dq_v}{dt} = -\frac{dq_l}{dt}, \quad (4)$$

where p , T , q_v and q_l are the pressure, temperature, water vapor mixing ratio, and liquid water mixing ratio of the parcel, $z(t)$ is the parcel height as given by (1), w the vertical velocity (dz/dt), p_e the environmental pressure, c_p and c_{pw} the specific heat at constant pressure of dry air and water vapor, respectively, g the acceleration due to gravity, and L_c the latent heat of condensation of water. These equations, and the microphysical equations which determine dq_l/dt , form a closed set.

The treatment of the microphysics involves only the condensational growth of cloud droplets (coalescence should be negligible for the range of cloud drop concentrations and sizes and cloud residence times involved in the calculations). Seventy-five distinct CCN sizes are treated with activation supersaturations ranging linearly from 0.04 to 1.52%. The CCN are composed of an insoluble, chemically inert particle of volume $5 \times 10^{-16} \text{ cm}^3$ and an appropriate amount of ammonium sulfate. (The final results would change little if the CCN were pure ammonium sulfate. Also, the neglect of giant nuclei with activation supersaturations $< 0.04\%$ is inconsequential.) Calculations are begun with the parcel at 100% relative humidity. Each CCN is in a solution droplet which is in equilibrium with the water

vapor pressure in the cloud parcel. As the parcel rises, the size of each droplet is adjusted to remain at equilibrium with the vapor pressure. If the activation supersaturations of any given CCN are reached, these CCN are activated and the growth of their associated droplets is calculated using the droplet growth model of Fukuta and Walter (1970).

Calculations have been made with a condensation level at -3°C and 600 mb. The initial cumulative CCN concentration spectrum used was $303(SS)^{0.6} [\text{cm}^{-3}]$ (where SS is the supersaturation in percent). The value of 0.6 for the index of SS is reasonable for maritime CCN distributions and the concentration at 0.5% supersaturation predicted by this relation (200 cm^{-3}) corresponds to many of Radke's observations. The maximum displacement of the parcel above its condensation level (Δh) was 150 m, giving a maximum liquid water content of about 0.25 gm kg^{-1} . As mentioned above, the velocity of this parcel at its condensation level (w_c) is a critical parameter for it determines the number of CCN activated. If, for example, the sulfate oxidation mechanism is to double the number of CCN active at 0.5% supersaturation, a sufficient number of drops in which the mechanism can proceed must be formed.

Fig. 2 shows the supersaturation in an air parcel as a function of time predicted by the model for several different updraft speeds; the CCN spectrum and cloud base parameters are as given above. Fig. 3 shows the maximum supersaturations attained, and the ratio of activated CCN to CCN active at 0.5% supersaturation, for different updraft speeds. Thus, for the oxidation mechanism to even have a chance of doubling the CCN

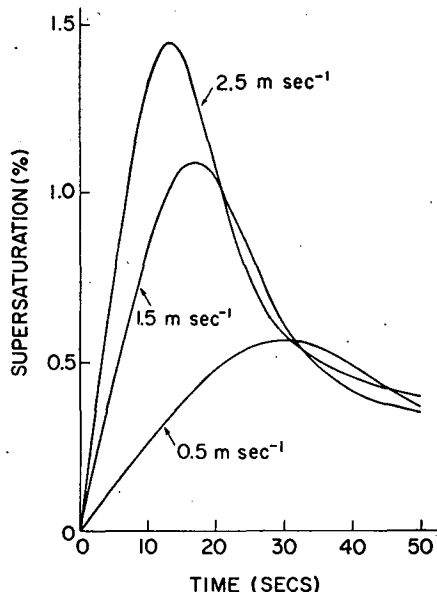


FIG. 2. Supersaturation in the wave cloud vs time for different updraft speeds at the condensation level. (The CCN spectrum and cloud base parameters are given in text.)

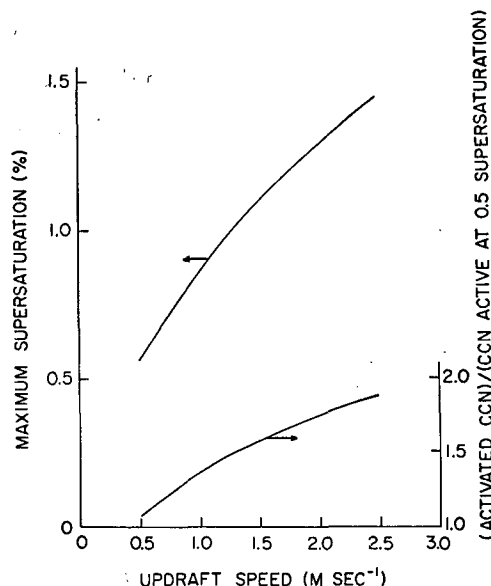


FIG. 3. Maximum supersaturations and activated CCN as a function of updraft speed.

active at 0.5% supersaturation, an updraft speed somewhat greater than 2.5 m sec^{-1} is required. The results presented in the following section are based on an assumed updraft of 2.5 m sec^{-1} . Radke did not measure updraft speeds. However, since updraft speeds well in excess of 2.5 m sec^{-1} have been measured on several occasions from our research aircraft flying over Mt. Rainier, our assumed value is probably conservative.

For a sinusoidal streamline such as that defined by (1), it may be shown that the range of times τ which a parcel spends above its condensation level is determined by $3.14 \leq (\tau w_c / \Delta h) \leq 4$. Thus, τ is limited by Δh and by w_c and must be large enough to activate sufficient CCN. In the calculations we take τ to be 240 sec.

The computation scheme for the cloud microphysics was as follows. Droplet growth was evaluated first, giving a change in the water vapor mixing ratio. The temperature change was then evaluated through (3) using this change in mixing ratio. Time steps for the integration of the microphysical equations were 0.5 sec for the first 20 sec of cloud time, and 2.5 sec thereafter. The chemical calculations, which are described below, were carried out only on activated CCN, and were begun once a CCN became activated. The time steps for integration of the chemical equations were 5 sec for the first 20 sec of cloud time, and 10 sec thereafter. The integrations were done sequentially: microphysics first followed by the chemical calculations.

b. The chemistry of the SO_2 - NH_3 -liquid H_2O system

The oxidation of SO_2 dissolved in cloud droplets first received attention from Junge and Ryan (1958)

whose experiments indicated that the oxidation was quite slow unless metal catalysts or ammonium ions were present in solution. They concluded that the reaction could explain some features of atmospheric sulfate formation.

Van den Heuval and Mason (1963) measured the rate of sulfate formation in drops exposed to equal pressures of SO_2 and NH_3 . The oxidation reaction in the absence of ammonia has since received attention (Miller and de Pena, 1972).

A mechanism for the oxidation of dissolved SO_2 was proposed by Scott and Hobbs (1967). They suggested that the oxidation of the sulfite ion is the rate-limiting process in the sulfate formation, and suggested a first-order rate equation of the form

$$\frac{d[\text{SO}_4^{2-}]}{dt} = k_3[\text{SO}_3^{2-}]. \quad (5)$$

Using the experimental results of Van den Heuval and Mason the value of the rate constant k_3 was evaluated, and calculations of sulfate production were made treating the SO_2 - NH_3 -liquid water equilibrium system in detail (see Appendix).

Calculations similar to those of Scott and Hobbs were made by McKay (1971). However, McKay used a value for the rate constant k_3 determined from experiments by Fuller and Crist (1941) which was more than ten times greater than the value used by Scott and Hobbs. McKay also considered the effects of temperature and the depletion of the SO_2 and NH_3 as the gases went into solution. The theoretical results obtained by both Scott and Hobbs, and McKay showed the oxidation to proceed at a rate large enough to be of significance in the atmosphere.

Miller and de Pena (1972) repeated the calculation with a value of k_3 close to that used by Scott and Hobbs, but they also considered the finite rate of the first dissociation of dissolved SO_2 into bisulfite. However, other experiments (Eigen *et al.*, 1961; H. Harrison, private communication) indicate that this dissociation is extremely fast, thus invalidating Miller and de Pena's calculations. (This does not, however, affect their evaluation of the oxidation rate k_3).

In the present paper we follow Scott and Hobbs' method for treating the SO_2 - NH_3 -liquid H_2O system. The chemical species considered in the liquid phase are H^+ , OH^- , $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , SO_3^{2-} , SO_4^{2-} , $\text{NH}_3 \cdot \text{H}_2\text{O}$, NH_4^+ , $\text{CO}_2 \cdot \text{H}_2\text{O}$ and HCO_3^- . (CO_3^{2-} can be neglected over the range of pH encountered in the calculations.) The reaction mechanism which is assumed to produce the SO_4^{2-} is the oxidation of SO_3^{2-} in the first-order reaction with a rate given by (5).

Table 1 shows values of k_3 used by different investigators. It can be seen that there is a considerable uncertainty and several questions remain to be resolved. Van den Heuval and Mason interpreted the results of their experiment in terms of liquid phase diffusion, but

TABLE 1. Values of the rate constant k_3 in Eq. (1) used by different investigators.

Investigator	k_3 at 25°C (sec^{-1})	Source
Scott and Hobbs (1967)	0.0017	Van den Heuval and Mason (1963)
McKay (1971)	$0.013 + 59[\text{H}^+]^{\dagger}$ (=0.032 at neutrality)	Fuller and Crist (1941)
Miller and de Pena (1972)	0.003	Miller and de Pena (1972)

simple calculations show that liquid phase diffusion should have been unimportant for the size of drops used in their experiment. Fuller and Crist's results show an unexplained dependence of the oxidation rate k_3 on the hydrogen ion concentrations, and also show no dependence of the oxidation reaction on the partial pressure of oxygen. In view of these uncertainties, our calculations were made with values of k_3 covering the range of values used by earlier investigators. An activation energy of $18.3 \text{ kcal mol}^{-1}$ (Barron and O'Hearn, 1966) was used to obtain the rate constant at varying temperatures.

Both Scott and Hobbs, and McKay assumed that the other reactions in the system (see Appendix) are fast enough, compared to the sulfate-producing reaction, to be treated on an equilibrium basis. With this assumption, the calculation of the increase of SO_4^{2-} with time is straightforward if fixed concentrations of SO_2 , NH_3 and CO_2 are specified. The electro-neutrality equation

$$[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + 2[\text{SO}_4^{2-}] + [\text{HCO}_3^-], \quad (6)$$

coupled with the equilibrium expressions, yields the following cubic equation for $[\text{H}^+]$:

$$[\text{H}^+] \left(1 + P_{\text{NH}_3} \frac{k_{ha}k_{1a}}{k_w} \right) = \frac{1}{[\text{H}^+]} (k_w + P_{\text{CO}_2} k_{hc} k_{1c} + P_{\text{SO}_2} k_{hs} k_{1s}) + \frac{2}{[\text{H}^+]^2} P_{\text{SO}_2} k_{hs} k_{1s} k_{2s} + 2[\text{SO}_4^{2-}], \quad (7)$$

where the various k values are defined in the Appendix. The concentration of SO_3^{2-} is then given by

$$[\text{SO}_3^{2-}] = \frac{P_{\text{SO}_2} k_{hs} k_{1s} k_{2s}}{[\text{H}^+]^2}, \quad (8)$$

and the concentration of SO_4^{2-} is found using a forward differencing technique, namely

$$[\text{SO}_4^{2-}]_{t+\Delta t} = [\text{SO}_4^{2-}]_t + \Delta t (k_3 [\text{SO}_3^{2-}]_t). \quad (9)$$

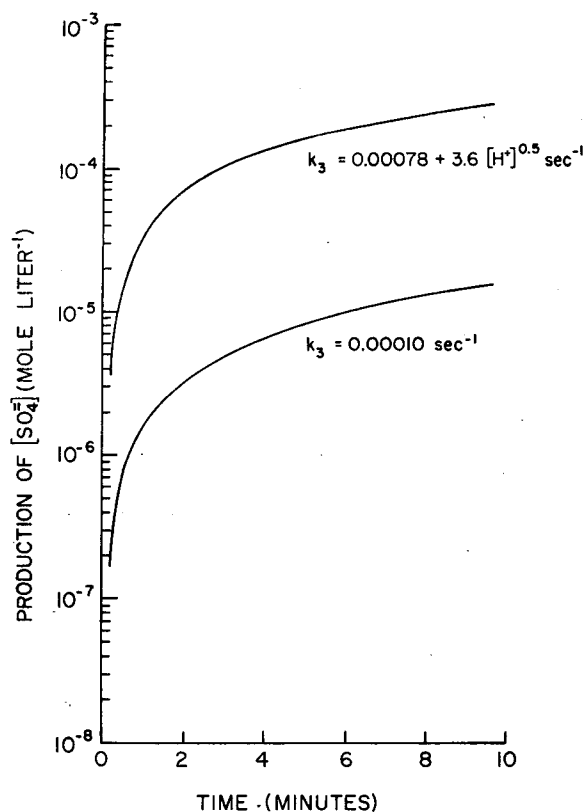


FIG. 4. Results of calculations of sulfate production in the SO_2 - NH_3 -liquid water system at 0°C , 600 mb total pressure and 311 ppm CO_2 . The concentrations of SO_2 and NH_3 in the ambient air are held constant at 1 and 3 ppb.

In all of the calculations the departure of the chemical system from ideal behavior is neglected. Certainly significant departures may occur at times shortly after nucleation or before final evaporation of a cloud drop. However, at such times the small amount of water in the droplet allows only insignificant changes in the mass of SO_4^{2-} .

The production of sulfates predicted by the above equations for the values of k_3 used by Scott and Hobbs and by McKay are shown in Fig. 4. In these calculations the concentrations of SO_2 and NH_3 in the ambient air were kept constant at 1 ppb and 3 ppb, respectively, which correspond to the concentrations of these gases in "clean" air.

For the wave cloud described earlier, the time-averaged mass of a cloud droplet is 3.3×10^{-10} gm. A CCN of ammonium sulfate with a 0.5% activation supersaturation dissolved in such a droplet gives a sulfate concentration of 2.9×10^{-6} mol liter $^{-1}$. The calculations shown in Fig. 4 indicate that it would take at most 2 min to produce such a concentration through the oxidation of SO_2 , so that the oxidation mechanism could easily account for CCN enhancement. However, the results shown in Fig. 4 cannot be used to predict the production of sulfates in wave cloud

droplets because they neglect the changes in the concentrations of SO_2 and NH_3 as the gases go into solution in the cloud droplets. In addition, the change of mass of sulfate in a droplet due to SO_2 oxidation depends on both $d[\text{SO}_4^{2-}]/dt$ and the mass of the droplets which are continually changing. Therefore, to predict CCN enhancement in a wave cloud the calculations must be done within the framework of a cloud model.

The transfer of sulfur and ammonia species to and in the cloud droplets is accomplished by gas and liquid phase diffusion. For the droplet sizes encountered in these calculations, diffusion processes are very fast compared to the sulfate oxidation reaction. This is easily shown for liquid phase diffusion, and the inclusion of gas phase diffusion into the calculations changes the sulfate production by less than 1%.

3. Results and discussion

Calculations were made using three values of the oxidation rate k_3 , namely, those used by Scott and Hobbs (1967), McKay (1971) and Miller and de Pena (1972), all adjusted to -3°C . The results are shown in Figs. 5, 6 and 8, where the initial cumulative CCN spectrum and the cumulative CCN spectrum after modification by the passage of the air parcel through the wave cloud are plotted. In addition, the cumulative

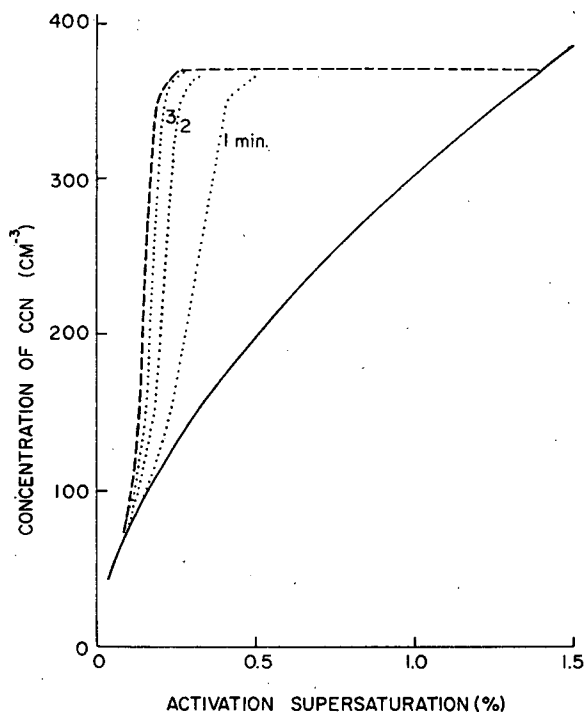


FIG. 5. Cumulative CCN spectra entering (—) and leaving (---) the cloud, and CCN spectra which would result if droplets were to evaporate after the air parcel had spent 1, 2 or 3 min in the cloud (.....). Oxidation rate k_3 after McKay. SO_2 and NH_3 concentrations, 1 and 3 ppb, respectively.

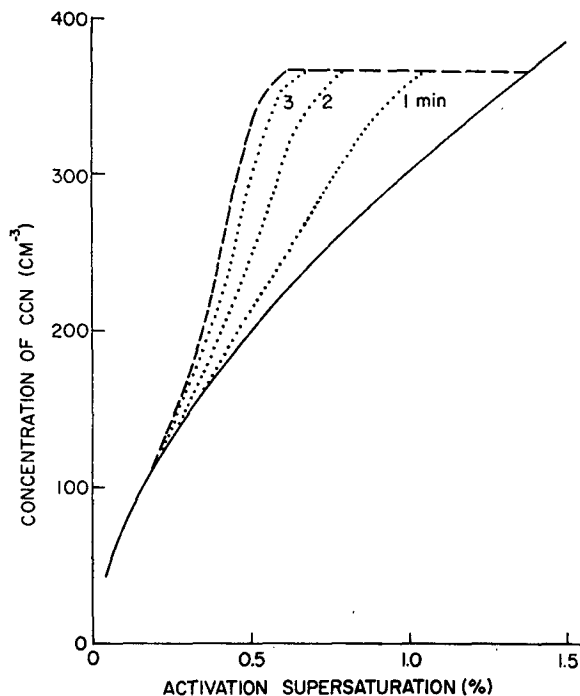


FIG. 6. As in Fig. 5 except for oxidation rate k_3 after Miller and de Pena.

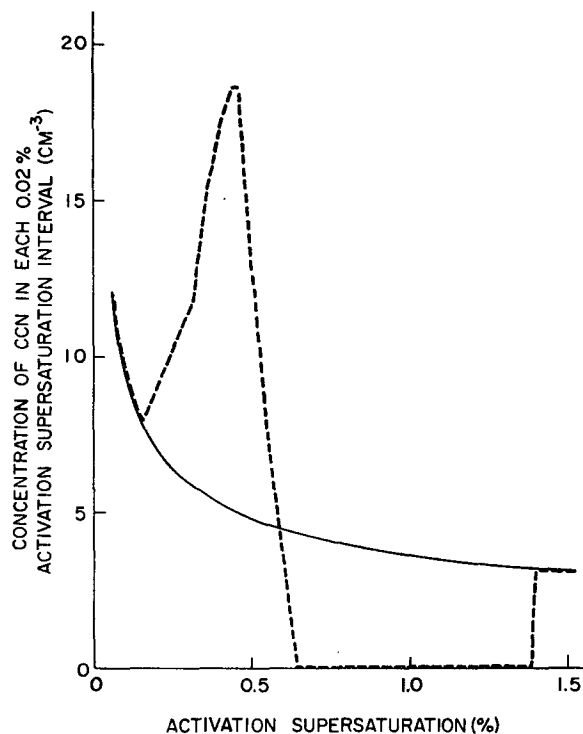


FIG. 7. Distributions of CCN with respect to activation supersaturation in air entering (—) and leaving (---) the wave clouds. Conditions are the same as for Fig. 6. (Note: this curve shows the concentration of CCN activated at a given supersaturation, whereas the cumulative CCN spectra in Figs. 5, 6 and 8 show the concentration of CCN activated at or below a given supersaturation.)

CCN spectra which would result if the cloud droplets in the air parcel were suddenly evaporated after the parcel had spent 1, 2 and 3 min in the cloud are plotted in these diagrams as dotted lines. In both cases the initial SO_2 and NH_3 concentrations in the air parcel are taken as 1 and 3 ppb, respectively, which are normal concentrations in clean air. Fig. 5 shows results obtained using McKay's value for k_3 . In this case, the sulfate production is so fast that after 1 min, each cloud droplet contains the amount of sulfate in an ammonium sulfate CCN active at 0.5% supersaturation. By the time the air parcel has left cloud, all the activated CCN have grown enough to be active at 0.25% supersaturation, and the number of CCN active at 0.5% supersaturation has increased by 84%. The mass of sulfate produced in this case was $0.31 \mu\text{g m}^{-3}$. (Complete oxidation of the 1 ppb SO_2 would produce $2.56 \mu\text{g m}^{-3}$ of sulfate.)

Fig. 6 shows results for the same conditions but using Miller and de Pena's value for the oxidation rate k_3 . In this case the number of CCN active at 0.5% increases by 64%. All of the activated CCN have grown enough to be active at 0.64% supersaturation. Fig. 7, which shows the distribution of CCN with respect to activation supersaturation in air entering and leaving the cloud for this case, clearly brings out the shift of CCN to lower activation supersaturations. The total sulfate produced in this case is $0.034 \mu\text{g m}^{-3}$.

Fig. 8 shows results for the same conditions but using Scott and Hobbs' value for the oxidation rate k_3 . In this case, there is only a 29% enhancement in the

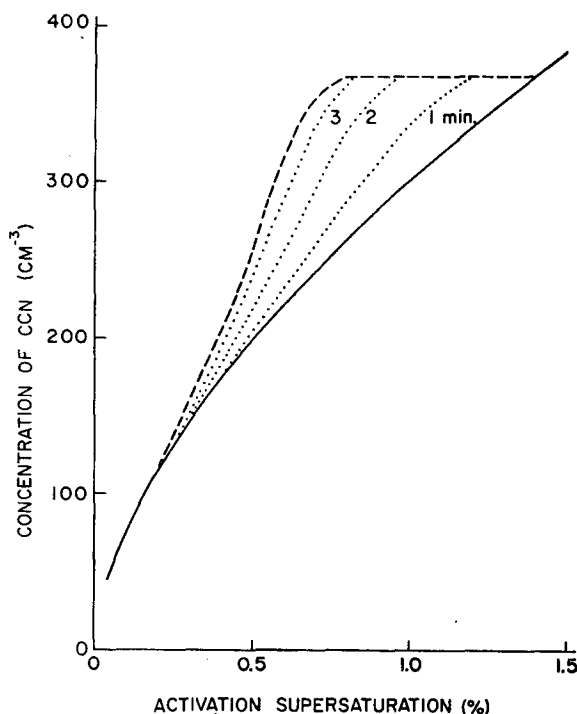


FIG. 8. As in Fig. 5 except for oxidation rate k_3 after Scott and Hobbs.

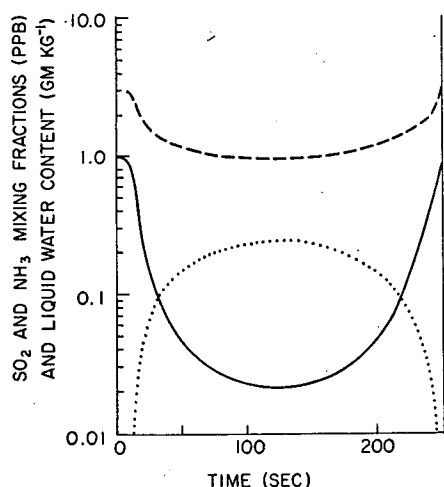


FIG. 9. Time variations of gaseous SO_2 (—), NH_3 (---), and liquid water (····) in the cloud parcel. (Conditions are the same as for Fig. 8.)

concentration of CCN active at 0.5% supersaturation after the air has passed through the cloud. This enhancement is significantly less than that predicted by calculations neglecting depletion of gaseous SO_2 and NH_3 (Fig. 4). The reason for this difference is seen in Fig. 9 which shows the changes with time of the mixing fractions of gaseous SO_2 and NH_3 and the liquid water content in the cloud parcel. As the SO_2 goes into solution in cloud droplets, its concentration in the air falls to 2% of its original value. Thus, the depletion of the trace gases in the cloudy air is very important. In this case $0.019 \mu\text{g m}^{-3}$ of sulfate was produced.

The above results show that the SO_2 oxidation mechanism can account for significant increases in CCN active at 0.5% supersaturation in small wave clouds of the type for which the calculations were made. With Scott and Hobb's oxidation rate there is only a 29% enhancement in the CCN active at 0.5% supersaturation. However, we tend to have more faith in the oxidation rates used by McKay and by Miller and de Pena since there are some ambiguities in Van den Heuval and Mason's experiments from which Scott and Hobbs derived their oxidation rate constant k_3 .

The model wave cloud used in the calculations seems representative of those observed by Radke, but one can consider how the results would be changed if the wave cloud parameters were varied. CCN enhancement will, of course, increase as the time a parcel spends in the cloud increases. (Although in the case of the calculation with the McKay oxidation rate, enhancement at 0.5% activation supersaturation is already complete.) Some of the clouds observed by Radke had parcel residence times on the order of 10 min. More enhancement is possible when more CCN are activated. This can occur through larger updrafts, or through having a CCN spectrum with a stronger supersaturation dependence. CCN spectra have not yet been measured during CCN enhancement incidents. Larger updrafts may exist but, as noted earlier, they should be associated with shorter residence times of the air parcel in the cloud and thus may produce less enhancement.

Calculations were also made to test the sensitivity of the CCN enhancement and sulfate production to the SO_2 and ammonia concentrations. Results for SO_2 concentrations of 1 and 3 ppb and ammonia concentrations of 3 and 6 ppb are summarized in Table 2. The results indicate that the sulfate production is fairly sensitive to the ammonia concentrations, showing a positive dependence as expected. The dependence of the sulfate production on SO_2 concentrations is rather surprising and is brought out further in Fig. 10 which shows results of calculations for SO_2 concentrations ranging from 1 to 10 ppm (the latter value may be found in polluted boundary layer air) and an ammonia concentration of 3 ppb. The sulfate production decreases with increasing SO_2 concentration. This is due to a reduction in the relative buffering capacity of the ammonia as more goes into solution with higher SO_2 concentrations, and a resulting rise in acidity and a decrease in the sulfite ion concentrations. Conditions which reduce the depletion of ammonia (e.g., smaller liquid water content, lower gas solubilities, and higher ammonia concentrations) will reduce or reverse the negative dependence of sulfate production on the concentration of SO_2 . Thus, in calculations which included depletion, McKay found the sulfate production increased with increasing SO_2 concentration.

TABLE 2. Effects of NH_3 and SO_2 concentrations on sulfate production and CCN enhancement.

SO_2 concentration (ppb)	NH_3 concentration (ppb)	Total sulfate produced ($\mu\text{g m}^{-3}$)			Increase in concentration of CCN active at 0.5% supersaturation (%)		
		McKay's oxidation rate	Miller and de Pena's oxidation rate	Scott and Hobb's oxidation rate	McKay's oxidation rate	Miller and de Pena's oxidation rate	Scott and Hobb's oxidation rate
1	3	0.31	0.034	0.019	84	64	29
1	6	0.36	0.046	0.026	84	79	44
3	3	0.47	0.033	0.018	84	61	27
3	6	0.84	0.079	0.044	84	84	74

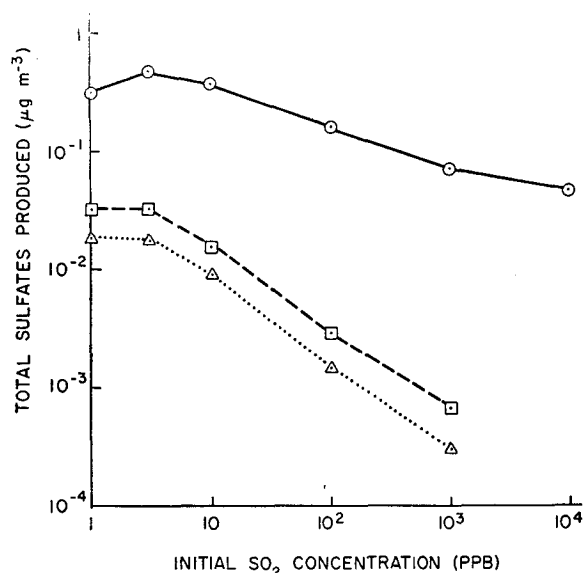


FIG. 10. Variation of total sulfate production with SO₂ concentration. Calculations made using oxidation rates after McKay (○—○), Miller and de Pena (□---□) and Scott and Hobbs (△····△). Ammonia concentration was 3 ppb.

The apparent significance of SO₂ oxidation in wave cloud situations leads one to speculate on its importance on a global scale. Friend (1973) has estimated that globally 1.33×10^{14} gm of sulfur leave the atmosphere as sulfates each year which enter the atmosphere in other forms (SO₂ or H₂S). Thus 4.2×10^{12} moles of sulfate are produced in the atmosphere annually. Global annual precipitation is about 5×10^{17} liters of water (Sellers, 1965). We will make the conservative assumption that only half the moisture which condenses in clouds is precipitated, so that over a year 10^{18} liters of water are present in clouds at one time or another. If one allows SO₂ oxidation to proceed for 15 min in this amount of cloud water, under typical atmospheric conditions (0°C, 750 mb, 0.5 gm kg⁻¹ liquid water, and SO₂ and ammonia concentrations of 1 and 3 ppb, respectively), then calculations based on the Scott-Hobbs mechanism discussed in this paper predict a total sulfate production of 6×10^{12} moles (using Miller and de Pena's value for the oxidation rate constant) or 4×10^{13} moles (using McKay's value for the oxidation rate constant). Thus, the oxidation of SO₂ in cloud drops appears well able to account for atmospheric sulfate production on a global scale.

4. Conclusions

A model has been developed which predicts the production of sulfates from oxidation of dissolved SO₂ in cloud droplets in small-amplitude wave clouds. The model considers the growth of the cloud droplets in an air parcel moving through the cloud and the simul-

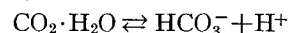
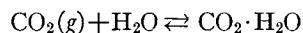
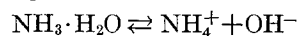
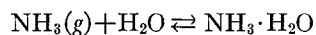
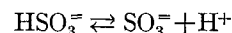
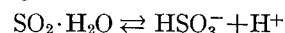
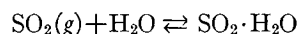
taneous production of sulfates through the Scott-Hobbs mechanism. The calculations indicate sulfate production much smaller than predicted by Scott and Hobbs (1967) and McKay (1971) due to the high depletion of SO₂ and NH₃ going into solution. Nevertheless, calculations in small wave clouds with ambient SO₂ and NH₃ concentrations representative of those in clean air predict that increases of about 75% in the concentrations of CCN active at 0.5% supersaturation can be produced by SO₂ oxidation. For the cloud conditions and NH₃ concentrations used, the sulfate production is found to be greatest at SO₂ levels near 1.5 and 3 ppb, with smaller sulfate production at larger SO₂ concentrations. This surprising result is due to the limited buffering capacity of the NH₃. Considering the importance of aqueous SO₂ oxidation in the global sulfur cycle, this would suggest that much more emphasis should be placed on measuring NH₃ concentrations, since small variations in NH₃ are as important as large SO₂ variations to the oxidation mechanism. Finally, a generalization of the SO₂ oxidation calculations to a global scale indicates that the Scott-Hobbs mechanism acting in cloud drops should be very significant in the worldwide conversion of SO₂ to sulfates in the atmosphere.

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APPENDIX

SO₂-NH₃-CO₂-Liquid Water System Reactions

The reactions in this system other, than the oxidation of SO₃⁻, and their associated equilibrium constants, as treated by Scott and Hobbs (1967), are as follows:



$$k_{hs} = [\text{SO}_2 \cdot \text{H}_2\text{O}] / P_{\text{SO}_2}$$

$$k_{1s} = [\text{H}^+][\text{HSO}_3^-] / [\text{SO}_2 \cdot \text{H}_2\text{O}]$$

$$k_{2s} = [\text{H}^+][\text{SO}_3^{2-}] / [\text{HSO}_3^-]$$

$$k_{ha} = [\text{NH}_3 \cdot \text{H}_2\text{O}] / P_{\text{NH}_3}$$

$$k_{1a} = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3 \cdot \text{H}_2\text{O}]$$

$$k_{hc} = [\text{CO}_2 \cdot \text{H}_2\text{O}] / P_{\text{CO}_2}$$

$$k_{1c} = [\text{H}^+][\text{HCO}_3^-] / [\text{CO}_2 \cdot \text{H}_2\text{O}].$$

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