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A Theoretical Study of the Wet Removal of Atmospheric Pollutants. Part II: The Uptake and Redistribution of $(\text{NH}_4)_2\text{SO}_4$ Particles and SO_2 Gas Simultaneously Scavenged by Growing Cloud Drops

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ABSTRACT

A theoretical model has been formulated which allows the processes which control the wet deposition of atmospheric aerosol particles and pollutant gases to be included in cloud dynamic models. The cloud considered in the model was allowed to grow by condensation and collision-coalescence, to remove aerosol particles by nucleation and impaction scavenging, and to remove pollutant gases by convective diffusion. The model was tested by using a simple air-parcel model as the dynamic framework. In this form the model was used to determine the fate of ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ particles and sulfur dioxide (SO_2) gas as they became scavenged by cloud and precipitation drops. Special emphasis was placed on determining 1) the evolution with time of the mass of total sulfur as S(IV) and S(VI) inside the drops, 2) the evolution with time of the acidity of the cloud water as a function of various oxidation rates and as a function of drop size, 3) the relative importance of sulfur scavenging from SO_2 as compared to sulfur scavenging from $(\text{NH}_4)_2\text{SO}_4$ particles, and 4) the effect of cloud drop evaporation on the aerosol particle size distribution in the air.

1. Introduction

In Part I (Flossmann et al., 1985) of a planned series of articles on the wet removal of atmospheric pollutants, we discussed the fate of water soluble and water insoluble aerosol particles scavenged by nucleation and impaction, involving cloud drops which grow by condensation and by collision and coalescence. This was done by means of a theoretical model in which—embedded in a dynamic framework—all relevant scavenging processes for aerosol particles were considered. In order to test our scavenging model, a simple air parcel model was used as the dynamic framework, although we stressed that at a later time, a two-dimensional (2-D) cloud dynamic model will be used as a more realistic dynamic framework. Because of the present simplification in the dynamic framework the applicability of the model to the real world was restricted, in that the model did not allow us to predict the rate at which aerosol material scavenged by a cloud is returned to the ground by wet deposition. On the other hand, the model *did* allow us to draw some important conclusions regarding the fate of the scavenged aerosol. In particular, the model allowed us to determine for in-cloud scavenging that 1) the scavenging of

aerosol particles by nucleation is of much greater importance than the scavenging by impaction; 2) during scavenging, aerosol particles are left unscavenged in the air as a drop-interstitial aerosol; 3) the scavenged aerosol material becomes redistributed in the cloud water during the collision and coalescence growth of the cloud drops; and 4) the mass mixing ratio of aerosol particles is large inside small drops, implying that smaller drops are more contaminated than larger ones. Qualitatively good agreement was obtained between the model predictions and field observations as far as they were available.

In the present study we have extended our earlier model and now consider aerosol particles as well as trace gases to be available for scavenging by the growing cloud drops. In this present model the aerosol particles were considered to consist of ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, while the gas was considered to consist of SO_2 . As in our earlier model, a parcel model was used as the dynamic framework, with the intention of formulating the scavenging model such that it may later be incorporated into a 2-D dynamic model for convective clouds. Due to the present simplified dynamics we again were restricted in our predictions. However, as we shall show here, the model *did* allow us to draw conclusions regarding 1) the relative importance of sulfur scavenging from SO_2 as compared to sulfur

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scavenging from $(\text{NH}_4)_2\text{SO}_4$ particles; 2) the redistribution which the sulfur, scavenged by the cloud drops from SO_2 and from $(\text{NH}_4)_2\text{SO}_4$, experiences during the collision and coalescence growth of cloud drops; 3) the amount of acid formed inside the cloud water; and 4) the effect of cloud drop evaporation on the aerosol particle distribution in the air.

Although a considerable number of field-, laboratory-, and theoretical studies have been performed on the general problem of scavenging of pollutant gases and aerosol particles by clouds and precipitation (for a review of past work see Walcek and Pruppacher, 1984a,b; Walcek et al., 1984; Flossmann et al., 1985), thus far only few contributions have been made to the four topics listed above. Thus, based on field measurements of SO_2 , sulfate particles in the air, and the amount of sulfate and acid found inside cloud water, Hegg and Hobbs (1981, 1982, 1983), and Hegg et al. (1984a) came to the conclusion that the efficiency with which sulfur is taken up by cloud drops through nucleation scavenging is considerably larger than the efficiency with which sulfur enters cloud drops via the uptake of SO_2 and subsequent oxidation inside the cloud water. In their study they deduced an inside cloud scavenging coefficient of 60% to 70%, on the average, for the uptake of sulfur from aerosol particles, thus attributing only 30% to 40% of the scavenged sulfur to the uptake and subsequent oxidation of SO_2 . Unfortunately, their measurements scattered widely so that no clear dependence on the amount of $(\text{NH}_4)_2\text{SO}_4$ and SO_2 present in the surrounding air, and on the rate of oxidation inside the cloud water could be determined. Also, no information was obtained on the variation with time of the efficiency of the two sulfur-uptake mechanisms. In addition, the field experiments did not allow any conclusions on the redistribution of the taken-up sulfur inside the cloud water due to collision and coalescence of cloud drops.

In a recent field study in Switzerland, Schumann et al. (1986) showed that inside-cloud nucleation scavenging is the dominant removal process, depleting more than 95% of the aerosol mass within approximately 1 h. Unfortunately, no measurements were made in this field study which could elucidate the contribution of gas scavenging to the overall removal of air pollutants.

Hegg et al. (1980) made field experiments on altocumulus lenticularis in order to study the "processing" of the taken-up aerosol and gas material inside cloud drops. They found that the uptake of SO_2 by cloud drops and the subsequent oxidation of SO_2 inside the drops to sulfate on the downwind side of the cloud where the drops evaporated, may tend to a significantly enhanced concentration of aerosol particles in the particle diameter range 0.5–3 μm , as compared to the concentration of these particles on the upwind side of the cloud where the aerosol particles condensed to drops. Since the newly formed aerosol particles were

found to be water soluble and hygroscopic, they acted as CCN, leading to a significant enhancement of the CCN concentration on the downwind side of the cloud as compared to the concentration on the upwind side. No theoretical confirmation is yet available on this finding.

Walcek and Pruppacher (1984b) applied their theoretical scavenging model to the scavenging of SO_2 in pollution layers *below a precipitating cloud* and determined for various conditions the amount of sulfur scavenged by falling rain. Unfortunately, their model did not allow them to make any statement on the amount of sulfur scavenged *inside the cloud*.

A number of numerical models are available in literature which treat the scavenging process by clouds using bulk parameterizations (e.g., Scott, 1982; Hegg et al., 1984b; Walcek and Taylor, 1986) or using analytical approximations (e.g., Hegg, 1983). Although such models are quite useful and, in fact, lead to some results which agree with those given in the present paper, the strength of the present model lies, in difference to the other models, in its explicit treatment of the cloud microphysics, which allows us to follow in a detailed fashion the material scavenged by the cloud from the moment of nucleation to the moment of rain drop formation.

This present model is described in section 2. In section 3, the cases chosen for evaluation are listed, and in section 4 the results of the numerical evaluation of the model are presented and discussed. In section 5 the main conclusions are summarized.

2. The present model

The present theoretical model is formulated in terms of a self-consistent set of equations to be used in conjunction with a model which describes the dynamic and thermodynamic input parameters for a convective cloud. However, as stated in section 1, it was decided to postpone a linkage with a 2-D cumulus dynamic model to a later time, and to test at present our scavenging model under simplified dynamic conditions, i.e., by linking it to an air parcel model which includes entrainment. The equations describing this air parcel model have been formulated and discussed by Flossmann et al. (1985) (Eqs. 22–31) and, for the sake of brevity, shall therefore not be repeated here.

Likewise, the relations for the time variation of the cloud drop number distribution function $f_d(m)$, the aerosol particle number distribution function $f_{\text{APa}}(m_{\text{AP}})$ for aerosol particles in air, the aerosol particle mass distribution functions $g_{\text{APd}}(m)$ for the aerosol in cloud water, the aerosol particle mass distribution function $g_{\text{APa}}(m_{\text{AP}})$ for the aerosol in the air, and the cloud drop mass distribution function $g_w(m)$, were discussed and evaluated, and their units given by Flossmann et al. (1985) (Eqs. 1–21). Therefore, these equations shall not be repeated here since they remain the same in the

present model. (The units of these functions are also given in the figures.)

In order to describe the uptake of SO₂ by the drops and any possible oxidation of the S(IV) to S(VI) inside the drops it became necessary to formulate and physically evaluate (in addition to the specified relations) relations for the time variation of the mass distribution functions $g_{G4d}(m)$ and $g_{G6d}(m)$ for S(IV) and S(VI) inside the drop, respectively, and the gas mass distribution function g_{Ga} for SO₂ in the air, where m is the mass of the drop which has been computed for the assumption that the mass of gas taken up by a drop does not contribute to an increase of the cloud drop radius. Furthermore, we assume that gas is not absorbed by unactivated dry and moist aerosol particles.

Analogously to the equations given by Flossmann et al. (1985) we then find the relations

$$\begin{aligned} \frac{\partial g_{G4d}(m)}{\partial t} = & -\nabla \cdot [v g_{G4d}(m)] + \nabla \cdot [K_m \nabla g_{G4d}(m)] \\ & + \frac{\partial}{\partial z} [V_\infty(m) g_{G4d}(m)] + \left. \frac{\partial g_{G4d}(m)}{\partial t} \right|_{\text{con/eva}} \\ & + \left. \frac{\partial g_{G4d}(m)}{\partial t} \right|_{AP,\text{coll}} + \left. \frac{\partial g_{G4d}(m)}{\partial t} \right|_{d,\text{coal}} + \left. \frac{\partial g_{G4d}(m)}{\partial t} \right|_{d,\text{break}} \\ & + \left. \frac{\partial g_{G4d}(m)}{\partial t} \right|_{\text{uptake}} + \left. \frac{\partial g_{G4d}(m)}{\partial t} \right|_{\text{ox}} \quad (1) \end{aligned}$$

$$\begin{aligned} \frac{\partial g_{G6d}(m)}{\partial t} = & -\nabla \cdot [v g_{G6d}(m)] + \nabla \cdot [K_m \nabla g_{G6d}(m)] \\ & + \frac{\partial}{\partial z} [V_\infty(m) g_{G6d}(m)] + \left. \frac{\partial g_{G6d}(m)}{\partial t} \right|_{\text{con/eva}} \\ & + \left. \frac{\partial g_{G6d}(m)}{\partial t} \right|_{AP,\text{coll}} + \left. \frac{\partial g_{G6d}(m)}{\partial t} \right|_{d,\text{coal}} + \left. \frac{\partial g_{G6d}(m)}{\partial t} \right|_{d,\text{break}} \\ & + \left. \frac{\partial g_{G6d}(m)}{\partial t} \right|_{\text{ox}} \quad (2) \end{aligned}$$

$$\begin{aligned} \frac{\partial g_{Ga}}{\partial t} = & -\nabla \cdot (v g_{Ga}) + \nabla \cdot (K_m \nabla g_{Ga}) \\ & - \int_0^\infty \left. \frac{\partial g_{Gd}(m)}{\partial t} \right|_{\text{uptake}} dm. \quad (3) \end{aligned}$$

In Eqs. (1) to (3) the terms $(\partial/\partial t)_{\text{con/eva}}$, $(\partial/\partial t)_{AP,\text{coll}}$, $(\partial/\partial t)_{d,\text{coal}}$ and $(\partial/\partial t)_{d,\text{break}}$ are due to the condensation growth or evaporation, the impaction scavenging of aerosol particles by drops, the collision and coalescence of drops, and the drop breakup, respectively. These were computed analogously to Eqs. (5)–(21) in Flossmann et al. (1985).

The remaining relations needed for formulating the model shall be considered for the case that *oxidation*

takes place inside the drops which have been nucleated on mixed (NH₄)₂SO₄ particles.

a. Drops of radius smaller than 30 μm

For drops of radius $a < 30 \mu\text{m}$, the computations of Walcek and Pruppacher (1984a, Fig. 11) show that the S(IV) in the water is in equilibrium with the SO₂ of the environment. For these drops we may therefore assume that all SO₂ taken up immediately becomes transformed into sulfur (VI) so that $\partial g_{G4d}(m)/\partial t = 0$. The increase of $g_{G6d}(m)$ can, therefore, be computed from the time-dependent diffusion equation. To do this we followed Walcek and Pruppacher (1984a, Fig. 10) and considered that for atmospheric SO₂ concentrations the main resistance to SO₂ diffusion lies in the gas phase. We felt justified to make this assumption, considering the relatively low values of SO₂ chosen to exist in an otherwise unpolluted atmosphere [with the exception of the presence of (NH₄)₂SO₄ aerosol particles], and for otherwise surfactant free water drops for which the sticking coefficient was assumed to be larger than 10⁻² (see also Walcek and Taylor, 1986). These authors note that as long as the sticking coefficient is larger than 10⁻² the equilibrium times for those species which ionize in solution are typically less than 1 μsec (Betts and Voss, 1970). Superimposed on these rapidly established equilibria are a series of slower irreversible reactions involving the oxidation of S(IV) to S(VI). For the previously given reasons we felt justified in disregarding resistance to diffusion inside the drop as considered, e.g., by Schwartz and Freiberg (1981). In addition, Walcek and Pruppacher (1984a) showed that the present treatment is consistent with the boundary layer treatment of Barrie (1978).

We may then write

$$4\pi a^2 D_g f_d(m) \frac{g_{Ga} - g_{\text{Gasurf}}}{\delta_g} = \frac{\partial g_{G6d}(m)}{\partial t} \quad (4)$$

where $\delta_g \approx a/F_v$, F_v is the ventilation coefficient for water vapor in air (see Pruppacher and Klett, 1978), which is a fair approximation for the ventilation coefficient of other gases (Baboolal et al., 1981). A linear conversion from S(IV) to S(VI) was assumed following the relation

$$\frac{\partial g_{G6d}(m)}{\partial t} = K' g_{G4d}(m) \quad (5)$$

where K' is the reaction rate constant for the conversion from S(IV) to S(VI). Since for pH ≤ 5.5

$$[\text{S(IV)}] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] \quad (6)$$

where with

$$c_g = [\text{SO}_2]_g$$

$$[\text{SO}_2 \cdot \text{H}_2\text{O}] = K_H c_g \quad (7)$$

$$[\text{HSO}_3^-] = K_1 K_H c_g / [\text{H}^+] \quad (8)$$

(see e.g., Walcek et al., 1984, Eqs. A2 and A4), we find for Eq. 6

$$[S(IV)] = K_H \left(1 + \frac{K_1}{[H^+]} \right) c_g, \quad (9)$$

from which

$$g_{G4d}(m) = K_H V_d f_d(m) \left(1 + \frac{K_1}{[H^+]} \right) g_{Gasurf} \quad (10)$$

and with (4) and (5)

$$g_{Gasurf} = \frac{4\pi a^2 D_g g_{Ga}}{\delta_g K' K_H V_d \left(1 + \frac{K_1}{[H^+]} \right) + 4\pi a^2 D_g}. \quad (11)$$

From Eqs. (4) and (5), $g_{G6d}(m)$ and $g_{G4d}(m)$ may be computed. And then

$$\left. \frac{\partial g_{Ga}}{\partial t} \right|_{\text{uptake}} = - \frac{\partial g_{G6d}(m)}{\partial t}. \quad (12)$$

b. Drops of radii larger than 30 μm

If drops growing by diffusion and collision and coalescence have reached radii larger than 30 μm they can no longer be considered to be in S(IV) equilibrium with the environment, considering a time step of 2 sec (see Walcek and Pruppacher, 1984a, Fig. 11). Instead, they have a sulfur (IV) concentration which, with increasing radius, increasingly lags behind the equilibrium value. The quantity $g_{G4d}(m)$ must therefore be computed from the time dependent diffusion equation:

$$\left. \frac{\partial g_{G4d}(m)}{\partial t} \right|_{\text{uptake}} = 4\pi a^2 D_g f_d(m) \frac{g_{Ga} - g_{Gasurf}}{\delta_g} - \left. \frac{\partial g_{G6d}(m)}{\partial t} \right|_{\text{ox}} \quad (13)$$

with

$$\frac{\partial g_{G6d}(m)}{\partial t} = K' g_{G4d}(m) \quad (14)$$

and

$$g_{G4d}(m) = K_H V_d f_d(m) \left(1 + \frac{K_1}{[H^+]} \right) g_{Gasurf}, \quad (15)$$

from which, again, g_{Gasurf} , $g_{G6d}(m)$, and $g_{G4d}(m)$, can be computed. The concentration of S(IV) and S(VI), respectively, are then given by

$$[S(IV)] = \frac{g_{G4d}(m)}{M_{\text{SO}_2} V_d f_d(m)} \quad (16)$$

and

$$[S(VI)] = \frac{g_{G6d}(m)}{M_{\text{SO}_2} V_d f_d(m)} + \frac{\epsilon g_{\text{APd}}(m)}{M_{(\text{NH}_4)_2\text{SO}_4} V_d f_d(m)}, \quad (17)$$

the latter equation being due to the presence of S(VI) from oxidized SO_2 as well as from ammonium sulfate. The change of SO_2 in the environment is then

$$\left. \frac{\partial g_{Ga}}{\partial t} \right|_{\text{uptake}} = - \frac{4\pi a^2 D_g f_d(m) (g_{Ga} - g_{Gasurf})}{\delta_g}. \quad (18)$$

The acidity of the cloud water and its $\text{pH} = -\log[H^+]$ was computed for all drop sizes from a set of five equations which also take into account that S(VI) is present due to the dissolved $(\text{NH}_4)_2\text{SO}_4$. Thus,

$$K_1 = \frac{[H^+][\text{HSO}_3^-]}{[\text{SO}_2 \cdot \text{H}_2\text{O}]}, \quad (19a)$$

analogous to Eq. (A6) of Walcek et al. (1984);

$$K_3 = \frac{[\text{SO}_4^{2-}][H^+]}{[\text{HSO}_4^-]}, \quad (19b)$$

analogous to Eq. (A17) of Walcek et al. (1984);

$$[S(IV)] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-], \quad (19c)$$

analogous to Eq. (A14) of Walcek et al. (1984);

and

$$[S(VI)] = [\text{SO}_4^{2-}] + [\text{HSO}_4^-], \quad (19d)$$

analogous to Eq. (A19) of Walcek et al. (1984).

In contrast to Eqs. (A13) and (A24) of Walcek et al. (1984) which only consider the uptake of SO_2 by pure water, the presence of $(\text{NH}_4)_2\text{SO}_4$ requires us to write the equation of electroneutrality as

$$[\text{NH}_4^+] + [H^+] = [\text{HSO}_3^-] + [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}]. \quad (19e)$$

In contrast to Eq. (A25) of Walcek et al. (1984), we therefore now obtain from the combination of Eqs. (19a-e) $[H^+]$ as an implicit function of S(IV) and S(VI):

$$[H^+]^3 + \{ (K_1 + K_3) - [S(VI)] + [\text{NH}_4^+] \} [H^+]^2 + \{ K_1 K_3 - ([S(IV)] - [\text{NH}_4^+]) K_1 - [S(VI)] (K_1 + 2K_3) + [\text{NH}_4^+] K_3 \} [H^+] - K_1 K_3 \{ [S(IV)] + 2[S(VI)] - [\text{NH}_4^+] \} = 0. \quad (19f)$$

3. Cases chosen for evaluation

For evaluating the model described in section 2, the drop size distribution was computed by assuming that the spectrum was determined by nucleation, condensation, collision and coalescence. The air parcel dynamics and the variation of the drop size spectrum were computed in a manner which closely followed the computations made by Flossmann et al. (1985). Through their activation to drops, aerosol particles were allowed to be consumed by nucleation scavenging. In addition, each drop was allowed to pick up aerosol particles by impaction scavenging with an efficiency specified in Flossmann et al. (1985). Furthermore, SO_2 gas mass was allowed to enter each drop via convective diffusion. During the growth of the drops by collision

and coalescence, the mass of aerosol and gas which was scavenged was allowed to be redistributed among the various drop size categories using the model as outlined in section 2. The dry size distribution of the aerosol particles subjected to nucleation and impaction scavenging was assumed to be described by a modified gamma distribution of the form given by Deirmendjan (1969):

$$f_{\text{APa}}(\ln r) = Ar^{\alpha+1} \exp(-Br^\gamma), \quad (20)$$

with $A = 2.5 \times 10^6 \text{ cm}^{-3} \mu\text{m}^{-3}$, $B = 15 \mu\text{m}^{-0.5}$, $\alpha = 1$, $\gamma = 0.5$, and for $N_{\text{APa}} = 590 \text{ cm}^{-3}$, gives a mass mixing ratio of $w_{\text{APa}} = 28.65 \mu\text{g m}^{-3}$.

As already pointed out in our earlier communication (Flossmann et al., 1985) our scavenging model cannot be applied in its present form to external aerosol mixtures, i.e., to aerosol particles existing side by side with different compositions. Instead, we assumed internal aerosol mixtures, i.e., aerosol particles all of which have the same composition of a given mass fraction ϵ . In our previous study (Flossmann et al., 1985) we had already determined the effect of various aerosol composition ϵ on aerosol particle scavenging. Therefore, we decided in the present study to assume that for all particles $\epsilon = 0.1$ [all particles consisting of $(\text{NH}_4)_2\text{SO}_4$ and some water insoluble material]. This was done to be consistent with field experiments (e.g., see Junge, 1963; Meszaros, 1981) which show that aerosol particles rarely consist entirely of $(\text{NH}_4)_2\text{SO}_4$. A value of $\epsilon = 0.1$ implies that for the previously given overall aerosol mass mixing ratio $w_{\text{APa}} = 28.65 \mu\text{g m}^{-3}$, the mass mixing ratio for ammonium sulfate becomes $2.865 \mu\text{g m}^{-3}$, equivalent to $2.08 \mu\text{g m}^{-3} \text{ SO}_4$ and $0.69 \mu\text{g m}^{-3} \text{ S}$.

We chose to apply our model to three different cases, A, B and C, (see Table 1). All three cases were evaluated using the equations specified in section 2 of this article using the numerical procedures outlined in Flossmann et al. (1985). The temperature and humidity distribution, and the initial updraft speed for the dynamic framework of the model were the same as those specified by Flossmann et al. (1985). As was shown by Flossmann et al. (1985), for the present conditions the model cloud did not reach levels below 0°C so that no ice phase developed.

For sulfur dioxide (SO_2) in the air we assumed a concentration of 1.0 ppb, equivalent to $3 \mu\text{g m}^{-3} \text{ SO}_2$

or $1.5 \mu\text{g m}^{-3} \text{ S}$. Comparing the present SO_2 mass in the air to that of the $(\text{NH}_4)_2\text{SO}_4$ aerosol mass we find a mole ratio [mol SO_2 to mol $(\text{NH}_4)_2\text{SO}_4$] of 2.15. The given specified concentrations for SO_2 and $(\text{NH}_4)_2\text{SO}_4$ are consistent with the observations of Isaac et al. (1986). The assumed values for the concentration of SO_2 are also consistent with the value given by Meszaros (1978), Perseke et al. (1980), Hegg and Hobbs (1982a,b) and Shaw and Paur (1983). The assumed values for the mass concentrations of sulfate in the air are consistent with the values given by Georgii et al. (1971), Meszaros (1978), Hidy et al. (1978), Brosset (1978), Hegg and Hobbs (1982a,b), Shaw and Paur (1983), and Hegg et al. (1984a).

Guidelines for the range of values assumed for the oxidation rate K' from S(IV) to S(VI) were obtained from Hegg and Hobbs (1978) and Martin (1984). The values chosen for K' were assumed to be constant over the whole computation time. This assumption is somewhat unrealistic as K' depends on pH, decreasing with decreasing pH for O_3 as oxidant, and increasing with decreasing pH for H_2O_2 Calvert et al. (1985). In the present computation we have not specified the oxidant but assumed that both may be present in the drop. Due to their opposite behavior with changing pH we felt justified to assume, as a first approximation, that the values for K' remain independent of pH, and therefore remain constant during the computation time. This assumption somewhat violates the fact that under atmospheric conditions the oxidant may significantly become depleted during the course of the in-cloud oxidation process (Walcek and Taylor, 1986). Again, we did not adhere in our model to any particular oxidant, and used rather small values for the SO_2 concentration. Therefore, we felt justified to treat K' as a pseudo first-order rate coefficient and to study its effect as a parameter on the overall sulfate and acidity production during the in-cloud scavenging mechanism.

4. Results and discussion

The results of case A are displayed in Figs. 1–7. Figures 1 and 2 give the time evolution of the drop size distribution in intervals of 200 sec. Drops are formed by condensation on aerosol particles and grow subsequently by collision and coalescence. The size evolution of the drops is documented in Fig. 1 by the number distribution function f_d as a function of drop radius, and in Fig. 2 by the water mass distribution function g_w as a function of drop radius. We notice from these two figures that the size distribution broadens quickly and develops precipitation size drops within about 20 min. Figures 3 and 4 exhibit the mass distribution functions for pollutants which entered the cloud water via aerosol particles and via SO_2 uptake, respectively. We notice the rapid redistribution of the entering particle and gas mass, respectively, inside the cloud water. This redistribution proceeds such that the main sulfur

TABLE 1. Input data for the three cases chosen for evaluation of the present model with $N_{\text{APa}} = 590 \text{ cm}^{-3}$, following size distribution Eq. (20).

Case	Amount of $(\text{NH}_4)_2\text{SO}_4$ mass in air [$\mu\text{g}(\text{NH}_4)_2\text{SO}_4/\text{m}^3$]	Amount of SO_2 mass in air ($\mu\text{g SO}_2 \text{ m}^{-3}$)	ppb	K' (sec^{-1})
A	2.865	3	1	5×10^{-3}
B	2.865	3	1	0.1
C	2.865	3	1	1.0

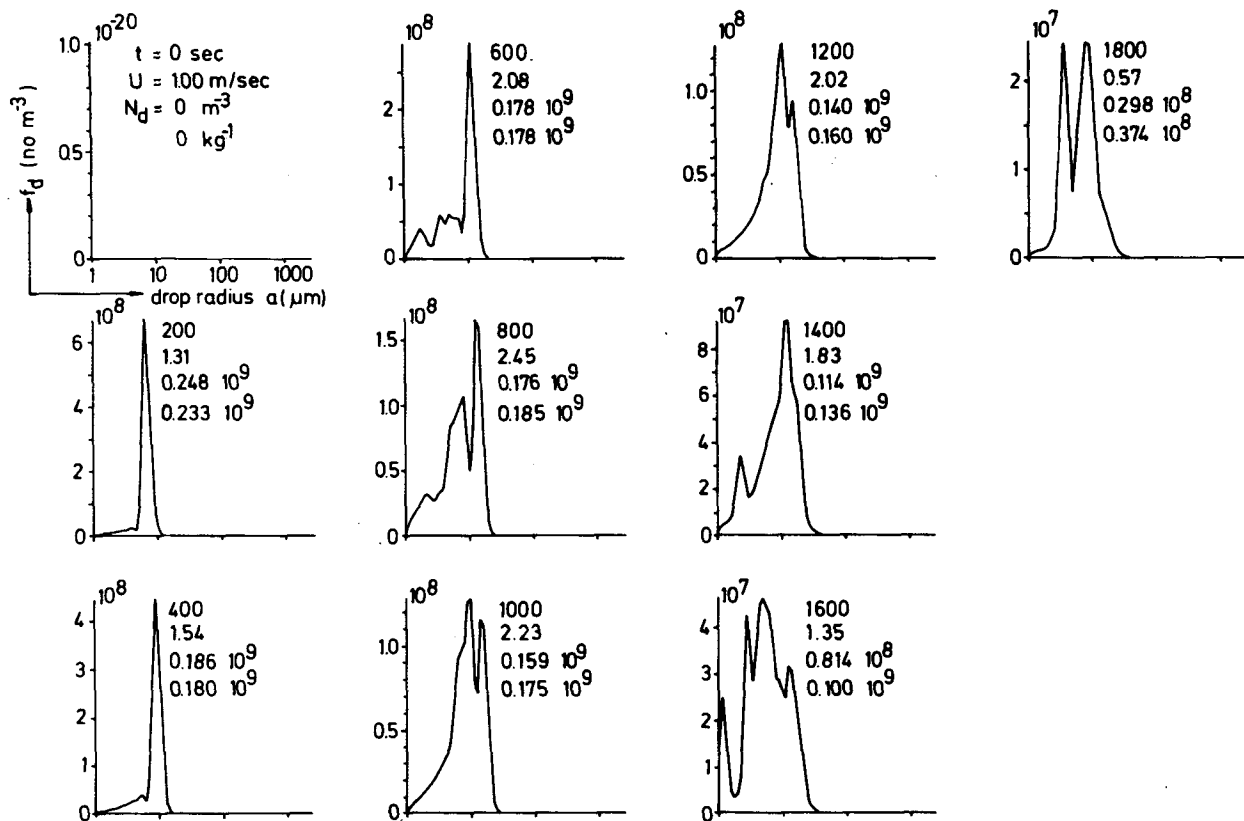


FIG. 1. Case A. Time evolution of the drop number distribution function f_d as a function of drop radius for the assumed initial size distribution of aerosol particles of assumed composition, which grow by condensation and collision-coalescence in an atmosphere of assumed vertical temperature and humidity distribution.

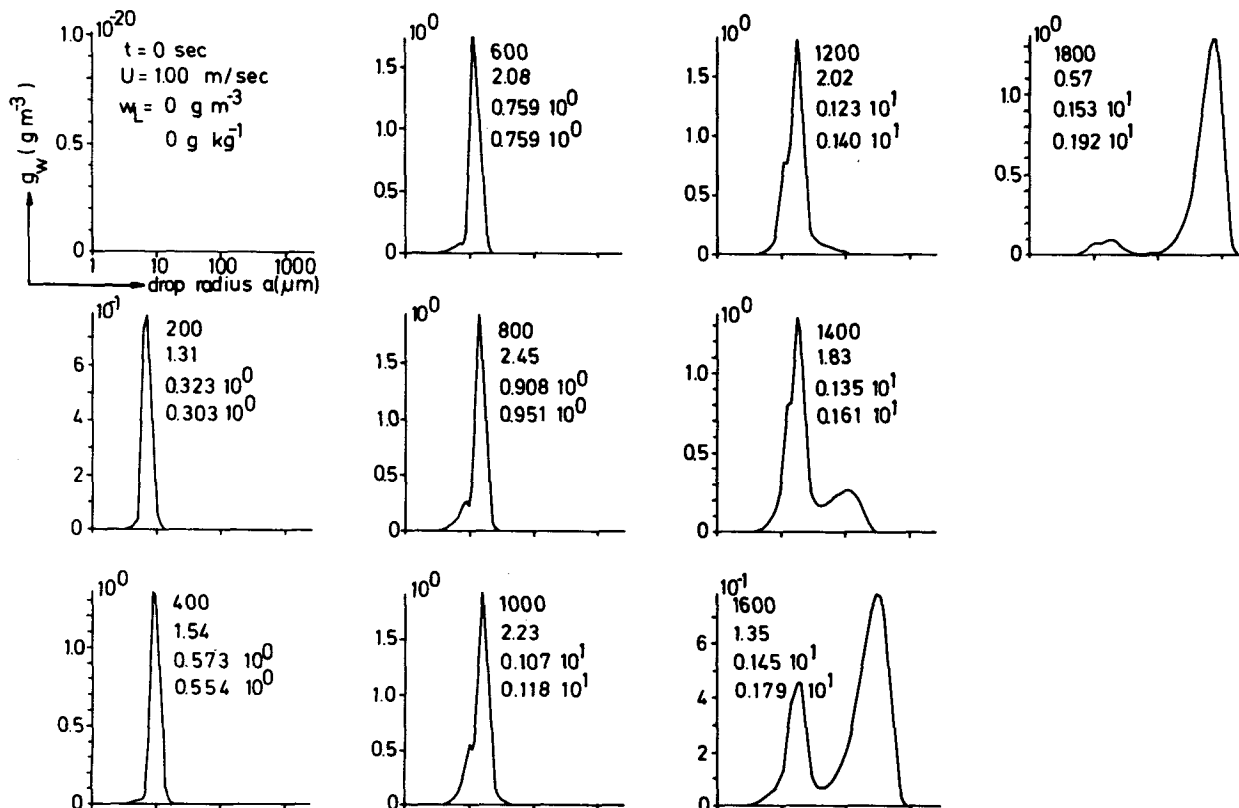


FIG. 2. Case A. Time evolution of the drop mass distribution function g_w as a function of drop radius for the conditions specified in Fig. 1.

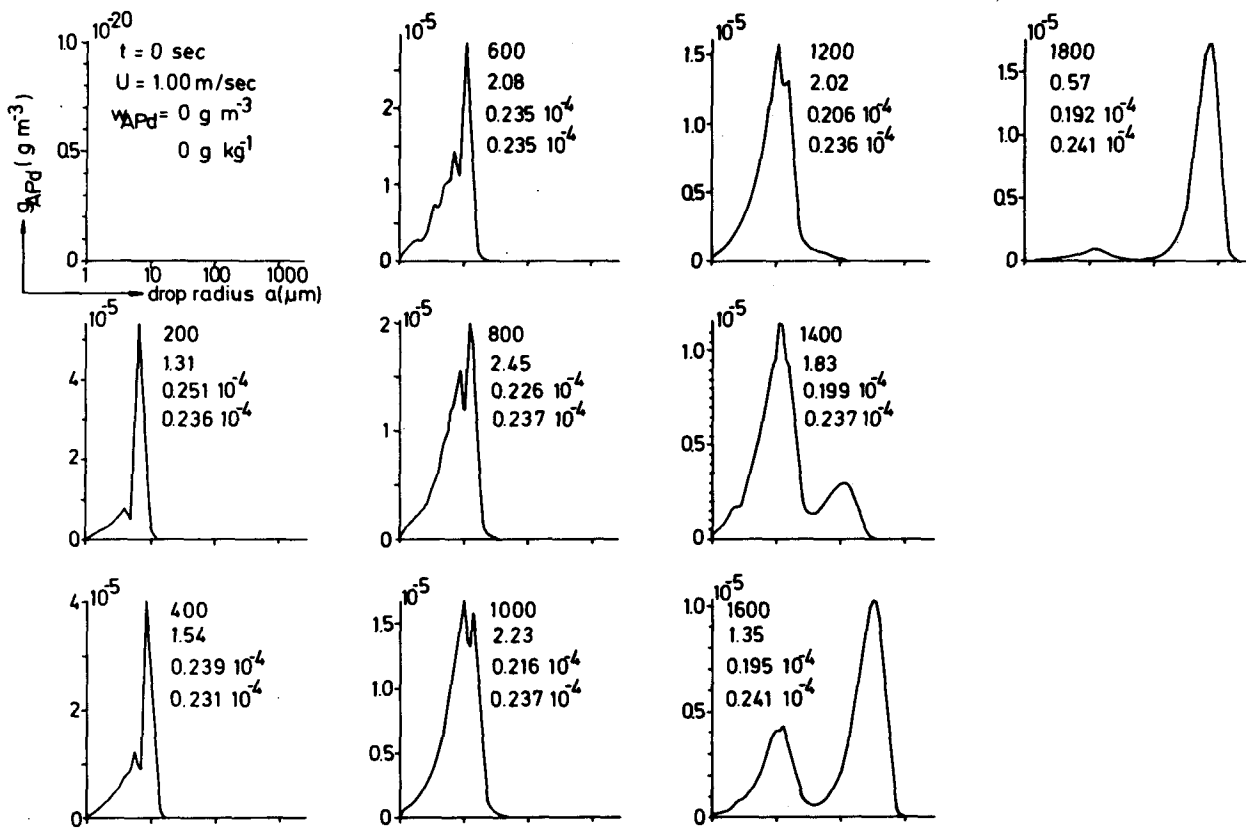


FIG. 3. As in Fig. 2, but for the aerosol particle mass distribution function g_{APd} for aerosol mass inside drops.

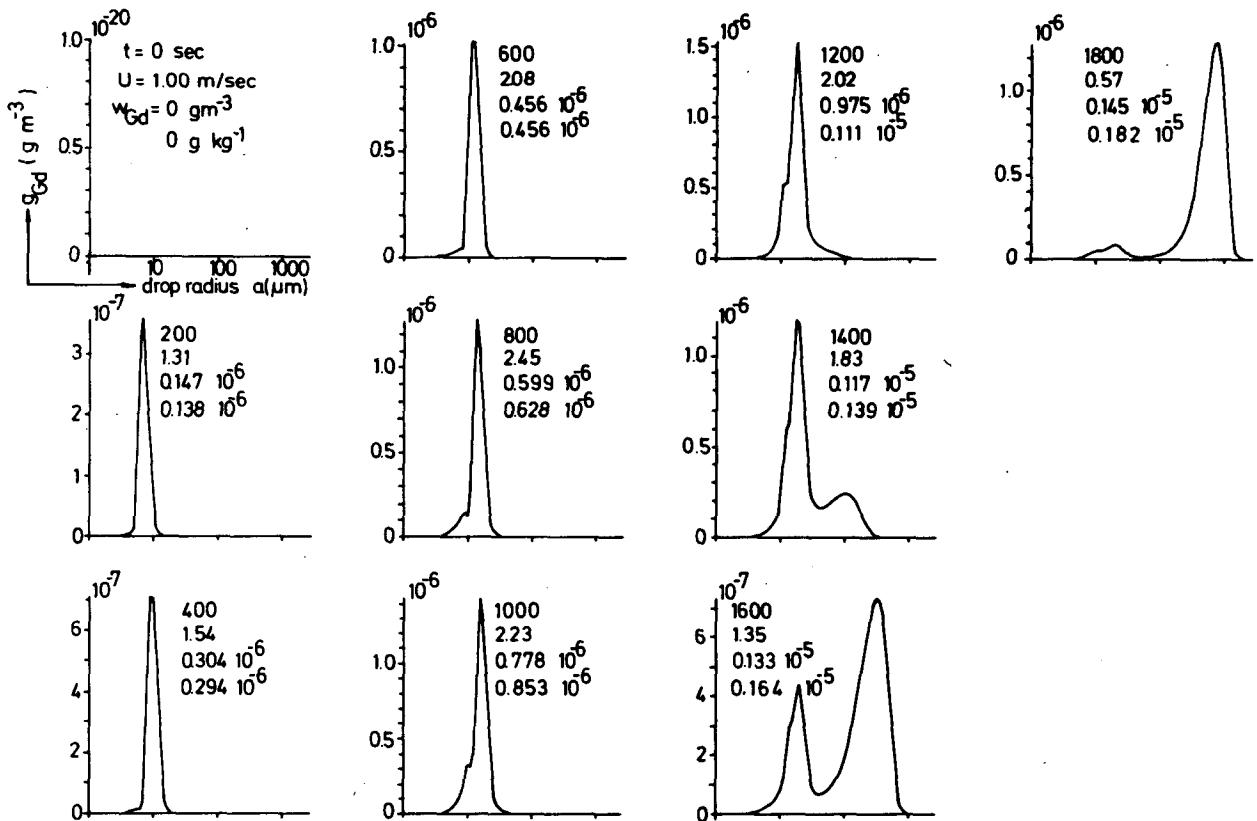


FIG. 4. As in Fig. 2, but for gas mass distribution function g_{Gd} for the mass of gas inside drops.

mass, whether it entered by uptake of aerosol particles or by uptake of SO₂, becomes associated with the main water mass, i.e., with the large precipitable drops.

In Fig. 5, the number distribution function for the aerosol particles in the air has been plotted as a function of time and aerosol particle size. We note from this figure that within the first 200 sec of the air parcels' life time, the aerosol particle concentration becomes reduced by 46% (equivalent to 2 orders of magnitude with regard to aerosol mass). Although a substantial number of aerosol particles remain as interstitial aerosol, they comprise only the very small sizes and therefore a practically negligible aerosol mass is scavenged by impaction. In Fig. 6, the concentration of sulfur (IV) which entered the cloud water by SO₂ uptake is given as a function of time and drop size. We notice from this figure that the S(IV) concentration *c*₄ decreases with increasing drop size, i.e. with increasing drop age and, thus, with increasing acidity H⁺ (decreasing pH), imposed on by Eq (9). By further growth due to water uptake by condensation, and collision and coalescence, the drops reach sizes at which, according to Walcek and Pruppacher (1984a, Fig. 11), they do not take up the equilibrium concentration of sulfur within the time-step interval of 2 sec used for describing the drop growth in our theoretical model. This "lag", together with the mixing of the drops, results in a fairly constant *c*₄ concentration for the drops larger

than 30 μm. From Fig. 7 we notice a totally different behavior for the concentration *c*₆ of sulfur (VI). The concentration *c*₆ passes through a maximum for drops of radii near 20 μm. This maximum is due to the fact that the small drops grow faster through condensation than they take up sulfur (IV) and convert it to sulfur (VI). Therefore, the smallest drops always also have the smallest S(VI) concentration. With increasing drop size, *c*₆ increases due to increasing drop age and thus longer oxidation times. The decrease of *c*₆ for drops larger than 20 μm is due to the lag in the *c*₄ concentration. With increasing time this minimum gradually fills up as the aging drops mix through collision and coalescence.

Due to the dissociation of the various sulfur species in water, hydrogen ions H⁺ are formed. These determine the pH = -log[H⁺] of the cloud water. We note from Fig. 8 that the pH of the drops generally decreases with increasing "drop age" and drop size. For case A, for which we assumed a moderate value for the oxidation rate *K'* = 5 × 10⁻³ sec⁻¹, our model predicts pH values which range from 5.5 to 4.5 after 30 min cloud life time. These values are reasonable with regard to the measurements of the acidity in rain water made by Georgii (1982), Perseke et al. (1980), Kins (1982) and others.

In Fig. 9 we have plotted the variation with time of the total sulfur per kilogram air which entered the drop

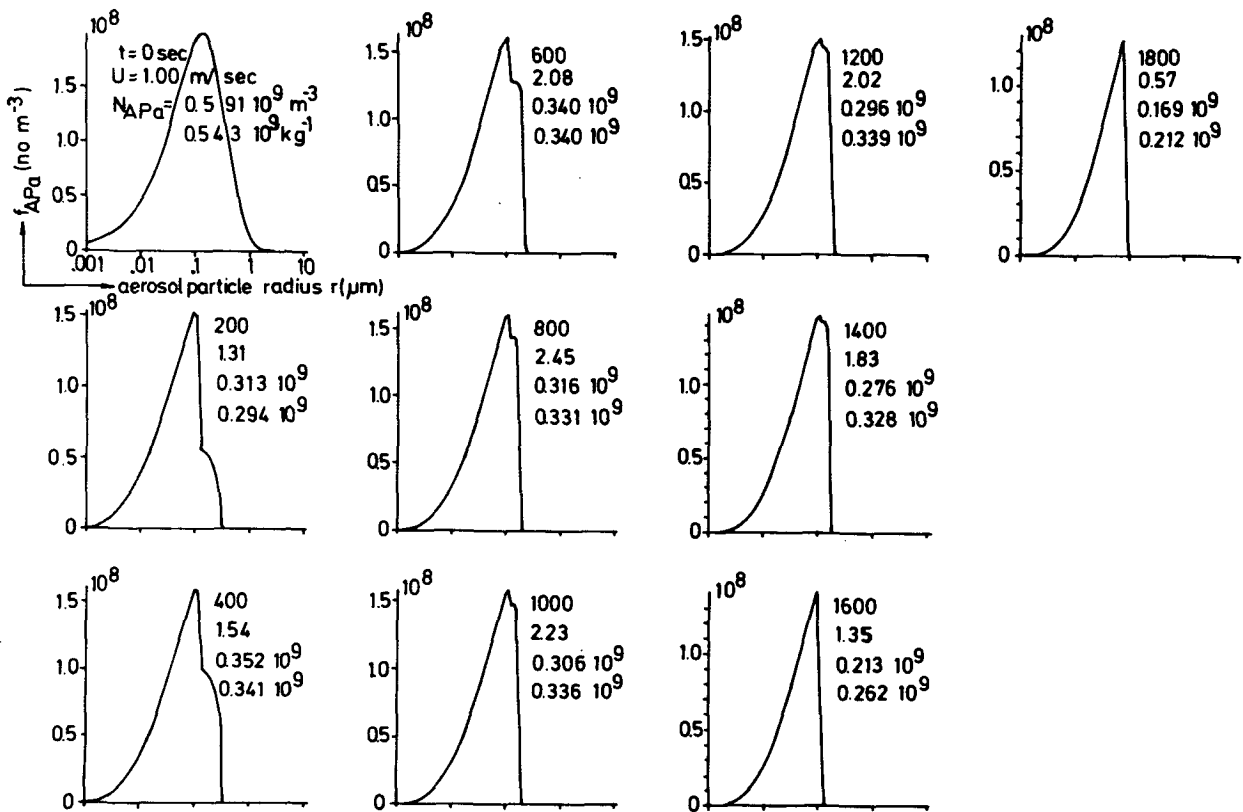


FIG. 5. As in Fig. 2, but for aerosol particle number distribution *f*_{APa} of aerosol particles in the air.

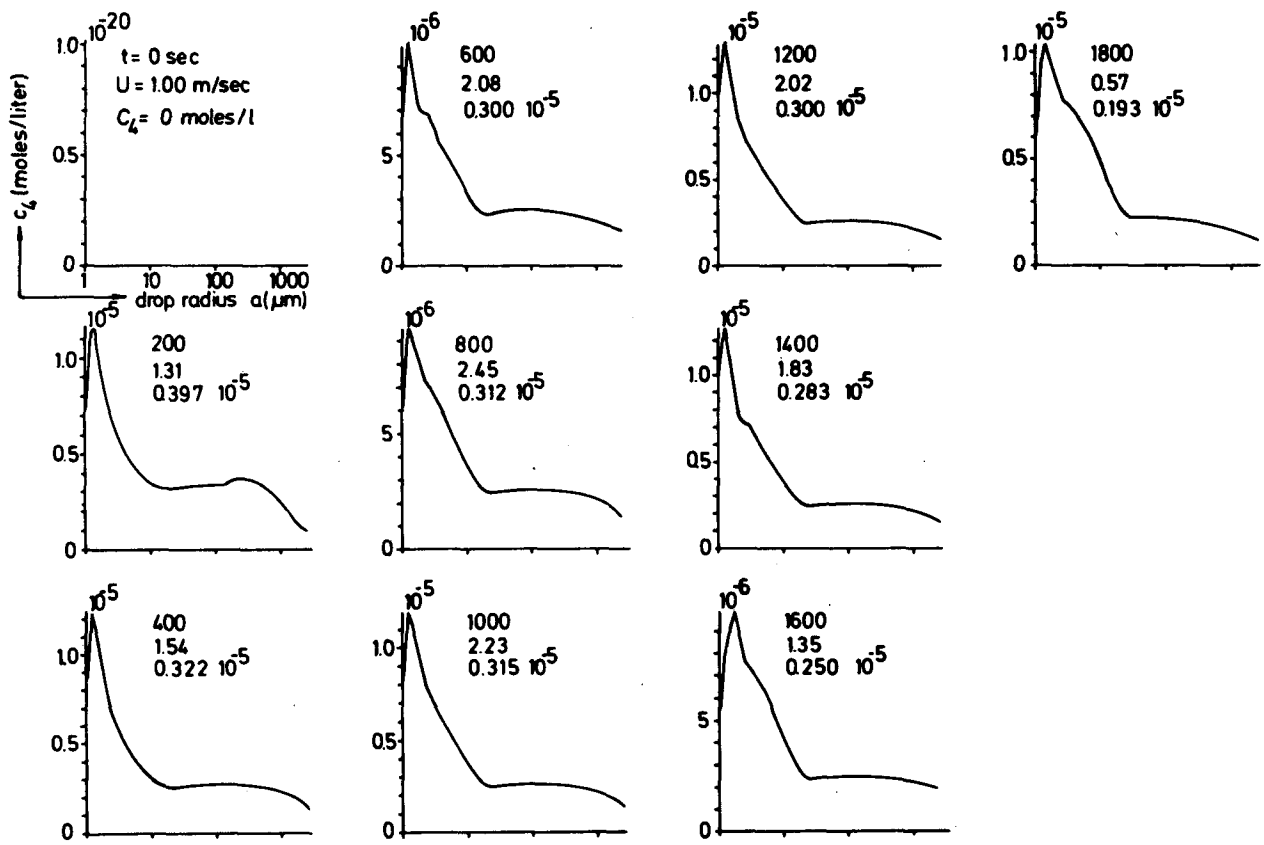


FIG. 6. As in Fig. 2, but for concentration c_4 of S(IV) inside drops.

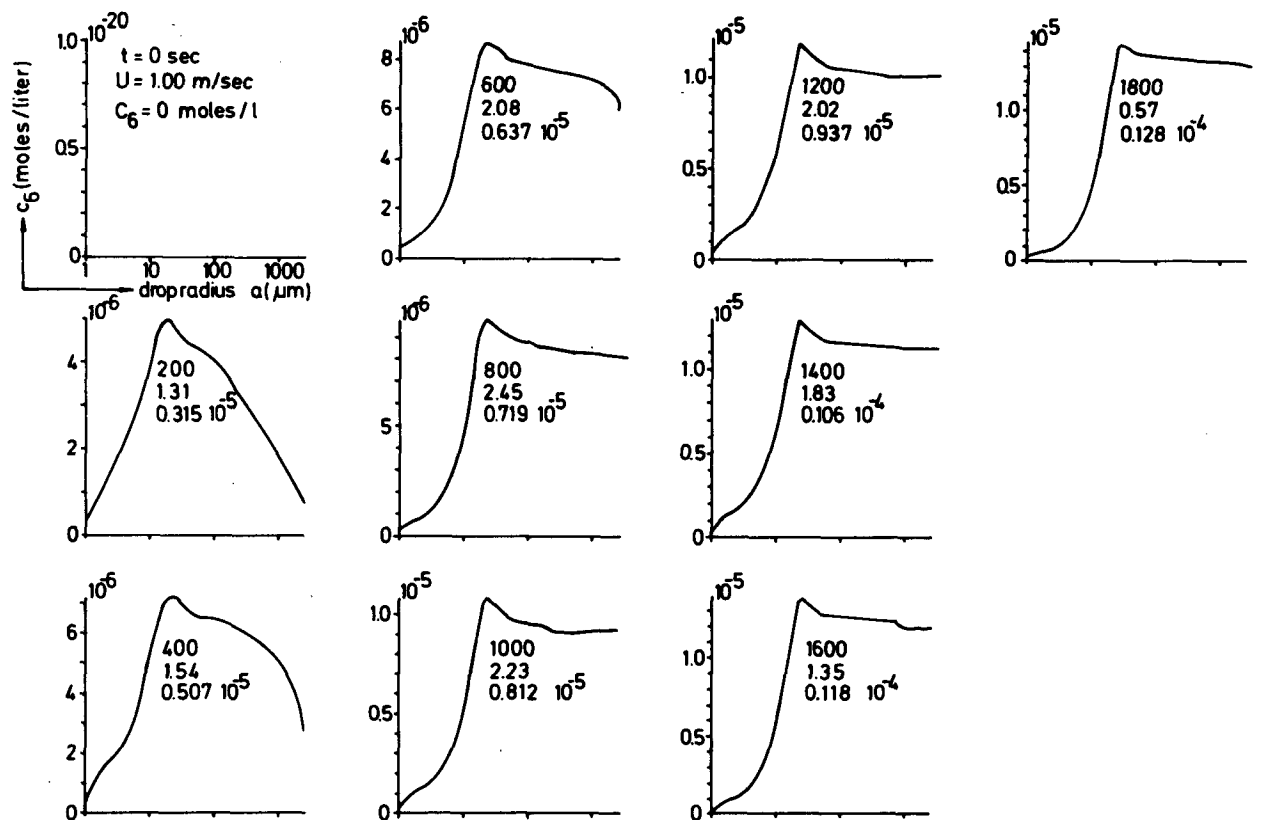


FIG. 7. As in Fig. 2, but for concentration c_6 of S(VI) inside drops.

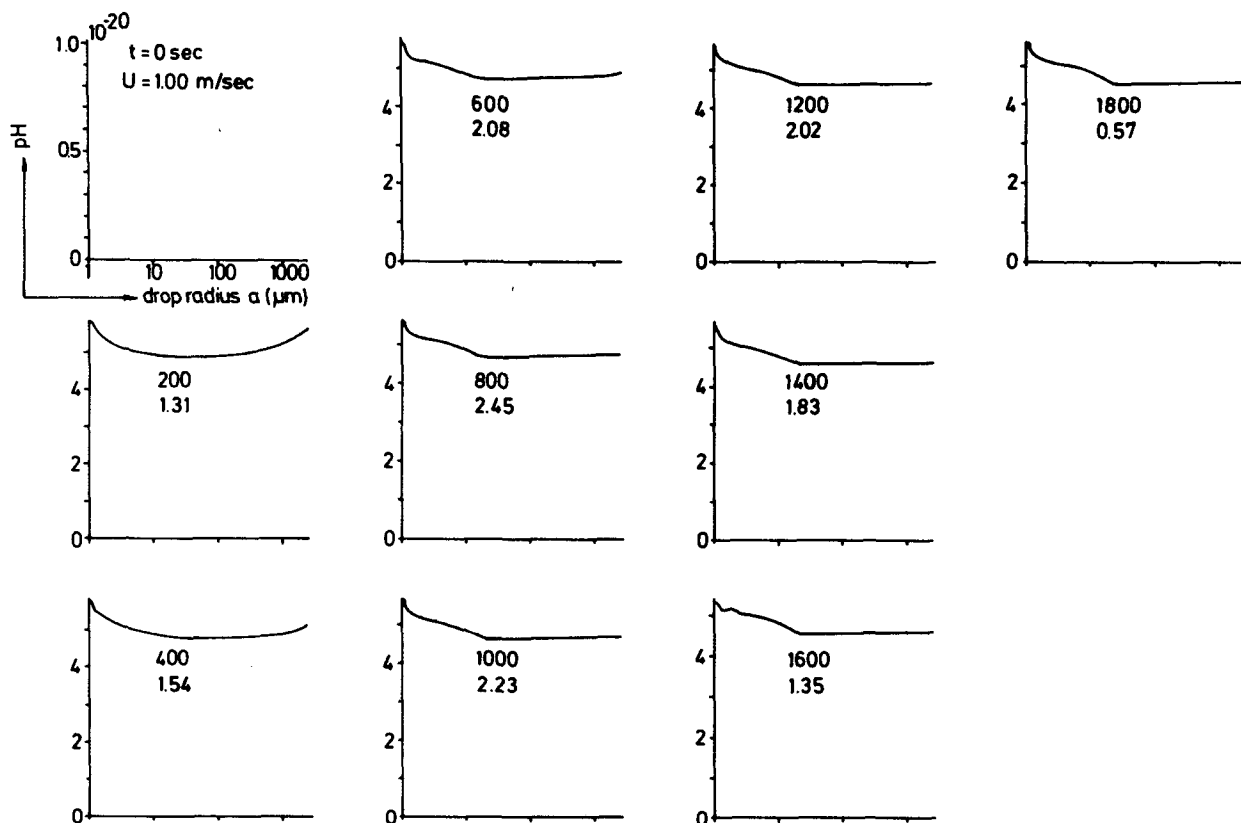


FIG. 8. As in Fig. 2, but for $\text{pH} = -\log[\text{H}^+]$ inside drops.

via aerosol particle scavenging and via the diffusion of SO_2 . We notice the immediate rise of the amount of sulfur due to nucleation scavenging. This amount is unperceptibly affected by condensation on aerosol particles which subsequently entered the cloud by entrainment, or entered the drops by impaction scavenging and therefore remains constant. In contrast, the amount of sulfur entering via SO_2 rises gradually with time as diffusion and oxidation proceeds. In the present cases A-C, the amount of sulfur entering via SO_2 sur-

passes the amount which entered due to aerosol particle scavenging after about 1200 sec for the case $K' = 5 \times 10^{-3} \text{ sec}^{-1}$, after about 450 sec for the case $K' = 0.1 \text{ sec}^{-1}$, and after 200 sec for the case K' is as large as 1.0 sec^{-1} . This latter fact is also illustrated in Fig. 10, which describes the time variation of the proportion which aerosol particle scavenging and gas scavenging contribute to the total sulfur scavenging. Both figures demonstrate that for a given gas and aerosol particle concentration, the oxidation rate is the major factor in determining the relative importance of the particle and gas scavenging mechanism. In the present study we used relatively low concentrations of SO_2 and $(\text{NH}_4)_2\text{SO}_4$. It is obvious that for increased percentage of $(\text{NH}_4)_2\text{SO}_4$, the curves labeled "aerosol particle scavenging" in Fig. 9 would shift upwards, causing the time after which gas scavenging dominates to become increasingly longer.

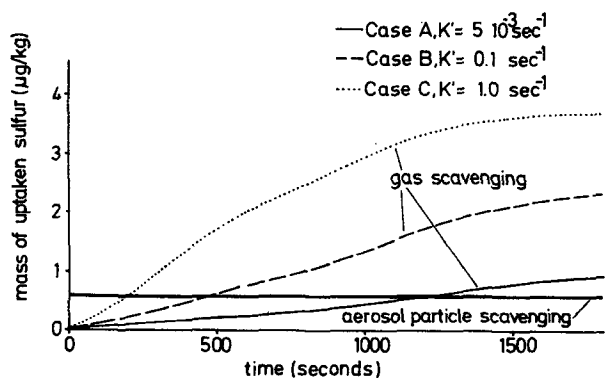


FIG. 9. Cases A, B and C. Time variation of the mass of sulfur taken up by aerosol particle scavenging of $(\text{NH}_4)_2\text{SO}_4$ and by gas scavenging of SO_2 .

In an attempt to compare our results displayed in Fig. 10 with field observations, we considered the data of Hegg and Hobbs (1982, 1983) who measured SO_2 concentrations in the air between 1 and 12 ppb(V) and sulfate as aerosol in air ranging between 0.5 and $10 \mu\text{g m}^{-3}$. Estimating from their data a mean value for K' of about 0.5 sec^{-1} , we deduce from Fig. 10 for a distance above cloud base equivalent to a computation time of 100 sec in our model, a percentage contribution of aerosol particle scavenging to the total scavenging of

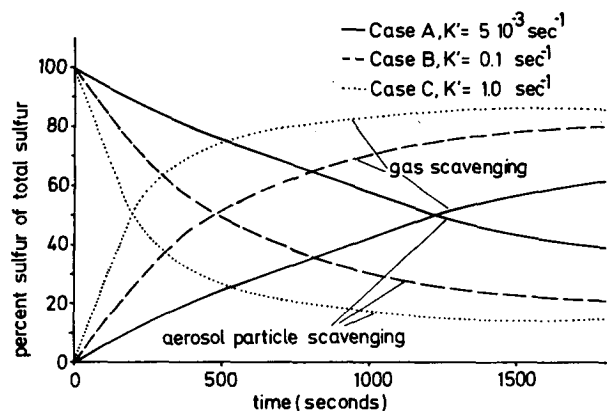


FIG. 10. As in Fig. 9, but for time variation of sulfur in percent of total sulfur.

sulfur of about 80%, and about 20% to gas scavenging. This agrees qualitatively with the estimate of Hegg and Hobbs (1983), whose estimated values for the percentage contribution of aerosol particle scavenging ranges for most cases between 53% and 77%.

In Table 2 we have compared the amounts of sulfur which had entered the cloud water via aerosol particles and via uptake of SO_2 after 30 min of cloud life time, as well as the pH of the cloud water at that time. Considering typical values published in literature which vary between 1 and 6 mg(S) per liter (Georgii, 1982; Kins, 1982; Perseke, 1982; Pruppacher and Klett, 1978; Meszaros, 1974, among others) we notice fair agreement between those values and our theoretically predicted values.

In Fig. 11 we have attempted to illustrate how a given aerosol particle spectrum (the aerosol particle spectrum used in the present computations) becomes "processed" during a condensation-evaporation cycle; this allows nucleation and impaction scavenging, gas scavenging and collision and coalescence between the cloud drops, and we assumed that the cloud evaporated after 30 min life time. We notice from this figure that after the cloud had evaporated, the aerosol particle distribution has become broader than the aerosol particle spectrum on which the cloud originated, implying that the number of aerosol particles which are able to become activated to drops in a second condensation cycle

TABLE 2. Amount of sulfur scavenged from $(\text{NH}_4)_2\text{SO}_4$ and SO_2 by cloud after 30 min of cloud life, for various oxidation rates.

Case	Amount of $(\text{NH}_4)_2\text{SO}_4$ in cloud water (mg S l^{-1})	Amount of SO_2 in cloud water (mg S l^{-1})	pH	K'
A	0.30	0.47	4.6	5×10^{-3}
B	0.30	1.20	4.2	0.1
C	0.30	1.91	4.0	1.0

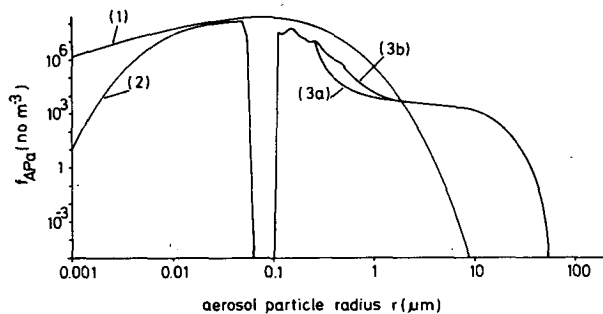


FIG. 11. Variation of the aerosol particle number distribution function f_{APa} for aerosol particles in air during a condensation-evaporation cycle; curve 1, original size distribution; curve 2, size distribution of cloud interstitial aerosol after 30 min cloud life time; curve 3, aerosol particle size distribution resulting after cloud has evaporated following 30 min lifetime: (a) aerosol particles for SO_2 absent; (b) aerosol particles for SO_2 present with $K' = 1.0 \text{ sec}^{-1}$.

has increased. This finding is in qualitative agreement with the field observations of Hegg et al. (1980).

In closing, we would like to emphasize that the present study only applies to aerosol particles of uniform composition. Nucleation scavenging may have different characteristics if the aerosol consists of particles of various chemical composition. We also considered the scavenging behavior for the case where, in addition to the aerosol particles, only one trace gas is present. Again, the uptake of this one gas may be considerably different in the presence of other trace gases, i.e., in the presence of gas mixtures. We finally would like to stress that the air parcel model only applies to in-cloud scavenging and cannot make any prediction regarding the amounts of aerosol particles and gas scavenged below the cloud. In order to investigate below-cloud scavenging we plan to apply the scavenging models to more sophisticated dynamic cloud models in the near future.

5. Summary and conclusions

The present study suggests for inside-cloud scavenging the following conclusions:

1) Collision and coalescence cause a redistribution among the cloud drops of the sulfur scavenged from SO_2 and $(\text{NH}_4)_2\text{SO}_4$. This redistribution takes place in such a way that the main sulfur mass is always associated with the main water mass in the cloud, i.e., it is contained in the larger drops which may reach the ground as precipitation.

2) In contrast to the sulfur scavenged solely from aerosol particles, which causes the smaller drops to be more contaminated than the larger ones, the concentration of sulfur scavenged from SO_2 is a function of time, concentration of SO_2 in the air, and oxidation rate of the sulfur in the drops. For the case that oxidation takes place in the drops, the sulfur concentration is generally larger in the large drops than in the small ones due to the age of the former, and to a longer time over which oxidation could be active. This also causes

the pH to be generally lower in the large drops than in the small ones.

3) For the typical SO₂ and (NH₄)₂SO₄ particle concentrations in the atmosphere it is found that SO₂ scavenging dominates the sulfur scavenging process, depending on the actual concentrations of these species in the air, the time in which the cloud drop is able to scavenge these species, and most of all, on the oxidation rate inside the cloud drops.

4) After the complete evaporation of a drop spectrum that scavenged gas and aerosol particles, the resulting aerosol particle spectrum has become broader than the aerosol particle spectrum on which the cloud originated. The newly formed aerosol particles are most likely also more effective as cloud condensation nuclei (CCN), thus enhancing the effectiveness of the spectrum to produce rain in a second cloud cycle.

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