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Chemical consequences of the initial diffusional growth of cloud droplets: a clean marine case

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ABSTRACT

A simple microphysical cloud parcel model and a simple representation of the background marine aerosol are used to predict the concentrations and compositions of droplets of various sizes near cloud base. The aerosol consists of an externally-mixed ammonium bisulfate accumulation mode and a sea-salt coarse particle mode. The difference in diffusional growth rates between the small and large droplets as well as the differences in composition between the two aerosol modes result in substantial differences in solute concentration and composition with size of droplets in the parcel. The chemistry of individual droplets is not, in general, representative of the "bulk" (volume-weighted mean) cloud water sample. These differences, calculated to occur early in the parcel's lifetime, should have important consequences for chemical reactions such as aqueous phase sulfate production.

1. Introduction

Howell (1949) noted that the growth of cloud droplets by water vapor diffusion causes the droplet size spectrum to narrow with time. This is a result of the tendency of smaller activated droplets to increase in radius more quickly than larger ones, allowing them to approach (but never reach) the size of the larger droplets.

Given the low supersaturations which exist in the atmosphere, droplets require a cloud condensation nucleus (CCN) in order to grow. Frequently this nucleus consists wholly or in part of water-soluble material which dissolves in the droplet, thus providing the compounds which, with the liquid water, determine the droplet's initial chemical composition. All droplets, as they grow by water vapor diffusion, will become progressively more dilute. Under these conditions, the smaller droplets, because of their higher surface area to mass ratio, will acquire more liquid water per unit mass and therefore become more dilute with time than their larger counterparts. This may be demonstrated mathematically as follows:

Solute concentration, C_s, is defined as the ratio of the number of moles (or mass) of a soluble substance to the volume of aqueous solution. If we define the mass of soluble substance present in a droplet to be m_s and the droplet volume to be V_d, then the relative change with time of droplet concentration is

$$\frac{1}{C_s}\frac{dC_s}{dt} = \frac{V_d}{m_s}\frac{d(m_s/V_d)}{dt}.$$

For a fixed solute mass, m_s, per droplet:

$$\frac{1}{C_s}\frac{dC_s}{dt} = -\frac{1}{V_d}\frac{dV_d}{dt}.$$

The droplet volume is proportional to the cube of the droplet radius, r_d, and the change in droplet mass or volume with time is proportional to the radius (see, e.g., Fletcher (1966)):

$$V_d \propto r_d^3; \quad \frac{dV_d}{dt} \propto r_d.$$

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Then the relative change in concentration with time is

$$\frac{1}{C_s}\frac{dC_s}{dt} \propto r_d^{-2}.$$

Thus the smaller droplets will dilute much more quickly than the larger ones.

In most tropospheric environments outside of clouds, there is a systematic dependence of aerosol particle composition with size (Whitby and Sverdrup, 1980). Coarse or "giant" particles of diameters greater than about 1 μm are mainly mechanically-produced substances like soil dust and sea-salt, and these are expected to act as CCN at low supersaturations. Smaller particles are usually the products of condensation from gaseous precursors. In the marine environment, the main condensation product is almost always H_2SO_4 that is partly neutralized with ammonia. These particles also have a composition and size range which make them suitable as CCN under realistic conditions. Thus, of those particles which act as CCN, the largest particles will contain different water-soluble matter than the smallest ones. Recently, Hudson and Rogers (1986) showed evidence that the largest droplets tend to form on the largest CCN and vice versa. Given the size-dependent composition of CCN and Hudson and Rogers' findings, the largest cloud droplets should not only have different chemical concentrations than the smaller droplets, but different solute species as well.

The variation in chemical composition of cloud droplets with time has been investigated by several researchers through integration of chemical models with increasingly complex dynamical cloud models. Scire and Venkatram (1985) explored sulfate production in droplets with a simple cloud model which included collision and coalescence processes, but did not use explicit microphysics to resolve the dependence of composition on droplet size. Walcek and Taylor (1986) investigated factors influencing vertical profiles of pH in cloud water in an entraining cumulus cloud but also did not resolve composition with size. The importance of aqueous phase sulfate production in a simple wave cloud was demonstrated by Hegg and Hobbs (1979), who showed that this process will occur more rapidly in some droplets than in others due to the pH variation of droplets activated at different supersaturations. Explicit microphysics which allowed prediction of variation in droplet pH with size were also used by Lee (1986) and Flossman et al. (1987). All these models, however, relied on an initial aerosol distribution which consisted only of an internal mixture, meaning all aerosol particles had the same chemical composition. Perdue and Beck (1988) considered exchange of gases with cloud droplets of varying pHs and the consequences of combining them into a bulk sample. While each of these papers dealt with some chemical aspects and in some cases with size-dependent composition, none of them addressed the consequences of nucleation on an external aerosol mixture (discussed below) or the general consequences of the dependence of chemical equilibrium on size. In this paper we have attempted to unify these points.

To investigate via computation the magnitude of the differences in solute concentration and composition among different sizes of droplets, we modeled a droplet population nucleating on an external marine aerosol mixture and growing by diffusion only. The use of an external mixture, (i.e., one in which all particles did not have the same chemical composition), was chosen to examine the possible chemical consequences of this type of mixture and because it is a more realistic representation (Whitby and Sverdrup, 1980; Bigg, 1980; Andreae, 1982) than an internal mixture assumption. The marine case was selected because it occurs over much of the globe and because an externally-mixed marine background aerosol can be defined in simple physical and chemical terms. The model is not intended to be all-inclusive and does not contain representations of processes such as entrainment and aqueous phase chemical reactions as do some of the works mentioned above. We consider the model sufficient to examine the consequences of the initial stages of diffusional growth upon an external aerosol mixture and to answer the following questions with respect to this process.

(1) How does the solute concentration and the chemical composition of droplets vary with size, and what is the range of concentrations that can exist? (More specifically, the pH and concentrations of major ions at chemical equilibrium were calculated for various droplet sizes.)

(2) Are there consequences of this size-depen-

dent chemistry for aqueous phase chemical reactions such as production of SO_4^{2-} by SO_2 oxidation?

(3) How does the chemical composition and concentration of individual droplets compare to that of the volume-weighted mean? (Liquid water sampled by bulk methods which collect droplets of all sizes together will have the volume-weighted mean composition, and cloud chemistry models usually incorporate only this composition into their reaction schemes.)

In addressing these questions, we are evaluating only the initial stages of cloud development, which sets the stage for all other cloud physical processes and chemical reactions.

2. Microphysical calculations

The cloud model used to calculate the droplet size spectrum was a one-dimensional Lagrangian parcel model with explicit heat and mass transfer equations given in Jensen and Charlson (1984). Because these equations are already published we will not reproduce them here. Since the model assumes adiabaticity, the results given in this paper are strictly applicable only to the initial diffusional growth near the base of a non-precipitating cloud. Balloon ascents in stratocumulus clouds in England have revealed near-adiabatic liquid water contents with narrow droplet spectra near cloud base (Slingo et al., 1982), and adiabatic cores have been observed even in cumulus clouds (Heymsfield et al., 1978; Jensen et al., 1985). Therefore, the results of these types of calculations may be considered realistic for many situations in the real atmosphere.

We examined the consequences of diffusional growth of droplets on a background marine aerosol which consisted of an externally-mixed ammonium bisulfate accumulation mode and a sea-salt coarse particle mode. This chemically simple aerosol, representative of the remote marine boundary layer, was chosen in order to look at the range of concentrations of the various species which exist in droplets nucleated on an external aerosol mixture (in this case, one in which the sulfate and sea-salt particles were not in physical contact with each other). Numerous measurements have verified that the major aerosol components (by mass) in unpolluted marine environments are sulfates and sodium chloride, and ammonium bisulfate was selected because the measured molar ratio of sulfate to ammonium ion is typically about one (Covert, 1988; Clarke et al., 1987; Duce, 1983; Charlson and Rodhe, 1982). Lognormal modal parameters as determined by Whitby (1978) for the input aerosol were fitted to number and mass concentrations measured by Clarke et al. (1978). The resulting mass distribution is shown in Fig. 1. 30 size classes were followed by the model for the accumulation mode and 24 for the coarse particle mode. The soluble fraction, ε, of both aerosol modes was equal to 1.0.

The initial sizes of the ammonium bisulfate and sea-salt aerosols were computed separately. Ammonium bisulfate particles were assumed to be in equilibrium with the environment at the 925 mb level (800 m) and a supersaturation (S) of -0.31%. The equilibrium assumption is justified because the time constant for a change in S is long relative to the time constant for droplet growth under these conditions (Jensen and Charlson, 1984). The growth calculation for the large sea-salt aerosols, which have a longer droplet response time, was begun at 938 mb with

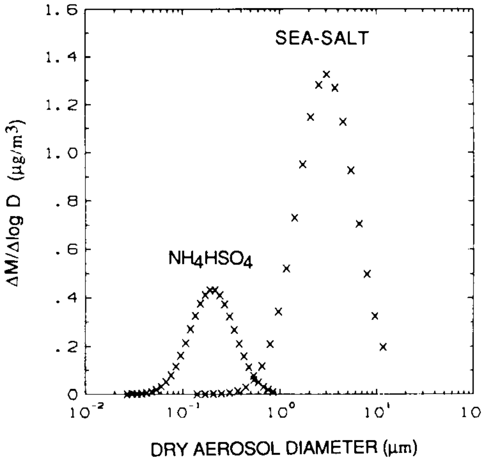

Fig. 1. Mass distribution of marine aerosol used in cloud model. Ammonium bisulfate accumulation mode had a total mass of 0.25 $\mu g\ m^{-3}$, a geometric mean diameter of 0.2 μg, a geometric standard deviation of 1.7, and a number concentration of 102 cm^{-3}. Corresponding values for the sea-salt coarse particle mode were 1.0 $\mu g\ m^{-3}$, 3.0 μg, 2.0, and 0.24 cm^{-3}, respectively.

$S = -6.15\%$. These droplets were raised adiabatically at a vertical velocity of 0.35 m s^{-1} to 925 mb ($S = -0.31\%$) and combined with the ammonium bisulfate aerosols. The cloud parcel in the model was then allowed to rise from the 925 mb to the 916 mb level (875 m) at a constant vertical velocity of 0.35 m s^{-1}. A 0.05 s time step was used for the 215 s model integration. (Droplet collision processes were assumed not to occur this early in the parcel's lifetime.) The peak value of S (0.56%) occurred at about 820 m altitude.

Droplet molarities as a function of cloud parcel height are shown in Fig. 2 (for the sulfate droplets) and 3 (for the sea-salt droplets). Each line represents the concentration history of an individual droplet size category, defined by the initial size of the dry aerosol particle. Below the cloud at 800 m, the molarity of a droplet in any sulfate category is determined by its CCN mass and its equilibrium size as dictated by the Köhler equation for that mass and supersaturation (in this case, -0.31%). The smallest droplets are initially (at equilibrium) more concentrated and appear farthest to the right on the horizontal axis. The X's represent the volume-weighted mean (or bulk) composition of all droplets shown in each figure.

Droplets in the very smallest sulfate categories (three lines farthest to the right in Fig. 2) remain as unactivated haze droplets and show little change in concentration with height except for a temporary dilution in response to the supersaturation peak at 820 m. The rapid growth and dilution by vapor diffusion of the smallest droplets that do activate is evidenced by a large decline in molarity between about 815 and 825 m altitude. In constrast, the largest droplets (more dilute than the smaller ones at pre-cloud equilibrium) dilute slowly, and therefore become more concentrated than the small ones at corresponding altitudes. At 875 m where the model was stopped, sulfate molarities of activated droplets span 3 orders of magnitude. Similar results occur for the sea-salt droplets in Fig. 3, with chloride concentrations in the larger droplets three orders of magnitude higher than in the smaller droplets at 875 m. (In the growth equations, the sea-salt was treated as sodium chloride, although the

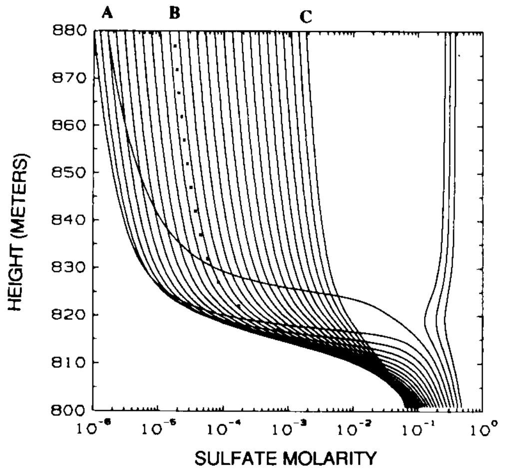

Fig. 2. Concentration history (with height or time) of 30 categories of droplets nucleated on ammonium bisulfate. At 800 m altitude, the small haze droplets are the most concentrated and the large are the most dilute, while within a few tens of meters above "cloud base" (0% S is at 808 m) the smallest activated droplets become the most dilute and the large ones become the most concentrated. Sulfate molarity spans 3 orders of magnitude for droplets over 1 μm in size. The X's represent the molarity of a bulk or volume-weighted mean sample of all the sulfate droplets; A, B, and C refer to categories whose composition is presented in Table 1.

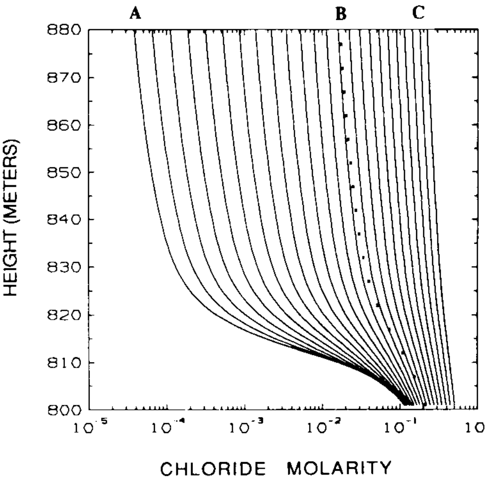

Fig. 3. Same as Fig. 2 but for droplets nucleated on sea-salt, showing again that the small droplets dilute faster with height. Here, the X's represent the molarity a sample would have if all sizes of only sea-salt droplets were collected. A, B, and C refer to categories whose composition is presented in Table 2.

Table 1. *Composition of sulfate droplets for selected size categories at 875 m*

	A (small)	*B (bulk)*	*C (large)*
droplet radius (μm):	4.4	N.A.*	8.5
dry radius (μm):	0.02	N.A.	0.42
pH:	5.3	4.8	2.5
$[SO_4^{2-}]$:	2×10^{-6}	2×10^{-5}	2×10^{-3}
controlling ions at equilibrium:	H^+ SO_4^{2-} HSO_3^- HCO_3^-	SO_4^{2-} NH_4^+ H^+	SO_4^{2-} H^+ (HSO_4^-)*•
[S(IV)]:	1.2×10^{-6}	3.0×10^{-7}	2.0×10^{-9}

Total liquid water in sulfate droplets = 0.125 g m^{-3}
• N.A. means not applicable for the bulk sample
** ( ) indicates minor contribution.

Table 2. *Composition of sea-salt droplets for selected size categories at 875 m*

	A (small)	*B (bulk)*	*C (large)*
droplet radius (μm):	6.9	N.A.*	28
dry radius (μm):	0.07	N.A.	4.8
pH:	5.5	6.7	7.3
$[Cl^-]$:	4.0×10^{-5}	1.7×10^{-2}	0.18
controlling ions at equilibrium:	H^+ HCO_3^- HSO_3^-	Ak^+ HCO_3^- HSO_3^- (SO_3^{2-})**	Ak^+ SO_3^{2-} (HSO_3^-) HCO_3^-
[S(IV)]:	2.0×10^{-6}	3.5×10^{-5}	3.2×10^{-4}

Total liquid water in sea-salt droplets = 0.001 g m^{-3}
* N.A. means not applicable for the bulk sample
** ( ) indicates minor contribution.

alkalinity of sea-salt was significant in the chemical calculations.) The letters on both plots refer to droplet categories for which additional data are given in Tables 1, 2 (discussed below).

3. Chemical calculations

In order to explore the chemical composition of individual droplet categories, the "master variable diagram" technique was used, as pioneered by Sillén (1967), and modified for simple application to cloud water by Vong and Charlson (1985). This assumes, as a first approximation, that cloud droplet growth processes are not affected by external trace gases and that droplets are in chemical equilibrium with the gases (here, SO_2 and CO_2). Under these assumptions, the ideal gas law, laws of mass action, Henry's law, mass continuity, and electroneutrality principles are used to calculate the equilibrium pH and ionic concentrations of droplets in a specific size category. Values of the equilibrium constants in the equations are taken at 278°K which was very nearly the air temperature (277°K) at 875 m calculated by the model. Although the equilibrium assumption is not always valid and additional chemical reactions such as oxidation of sulfur (IV) species may take place during rapid droplet growth, this approach is useful in describing the overall tendency of the system. It allows us to determine which chemical species are dominant in controlling the chemical equilibria and to predict what reactions are most likely to occur.

We selected two individual droplet categories

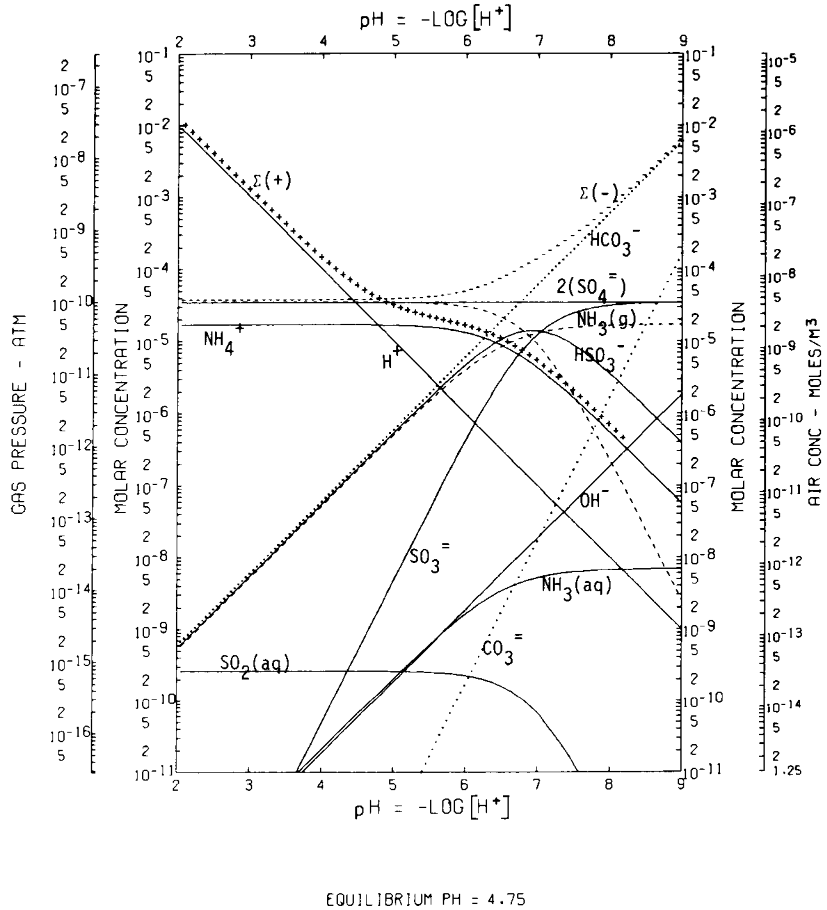

Fig. 4. Master variable diagram for the bulk sulfate sample at 875 m altitude. Equilibrium pH occurs where $\Sigma-$ charges $= \Sigma+$ charges. Input conditions are 0.206 μg m^{-3} sulfate ion and 0.0386 μg m^{-3} ammonium ion, 0.1 ppb sulfur IV (SO_2), 0.125 g m^{-3} liquid water, 340 ppm CO_2, and 278°K.

(one containing large droplets and one containing small ones) as well as a bulk sample for each of the droplet types at 875 m in the cloud for analysis by this technique. For simplicity, concentrations of soluble gases were set at 0.1 ppb SO_2 and 340 ppm CO_2. At these levels, examination of the master variable diagrams indicated that most (>99%) of the SO_2 was in the gas rather than the aqueous phase and therefore, all droplet categories could be considered to be surrounded with a uniform 0.1 ppb of the gas. In addition, the ammonium ion was assumed to remain distributed as it had been in the pre-cloud particles and exchange of ammonia between droplet categories was neglected, which is reasonable for these liquid water contents and very low gas phase NH_3 concentrations. This implies that different droplet sizes would have different NH_3 vapor pressures but that gas phase concentrations would be so low that no exchange would actually occur.

Droplets nucleated on NaCl were assumed to contain alkalinity from seawater, diluted in exact proportion to chloride ion concentration. Thus the alkalinity, Ak^+, in Fig. 5 and Table 2 was calculated from the known alkalinity and chlorinity of sea water (2.3 × 10^{-3} and 0.55 molar, respectively, from Stumm and Morgan (1970)) and the droplet chlorinity resulting from the cloud model calculations. The model also computed

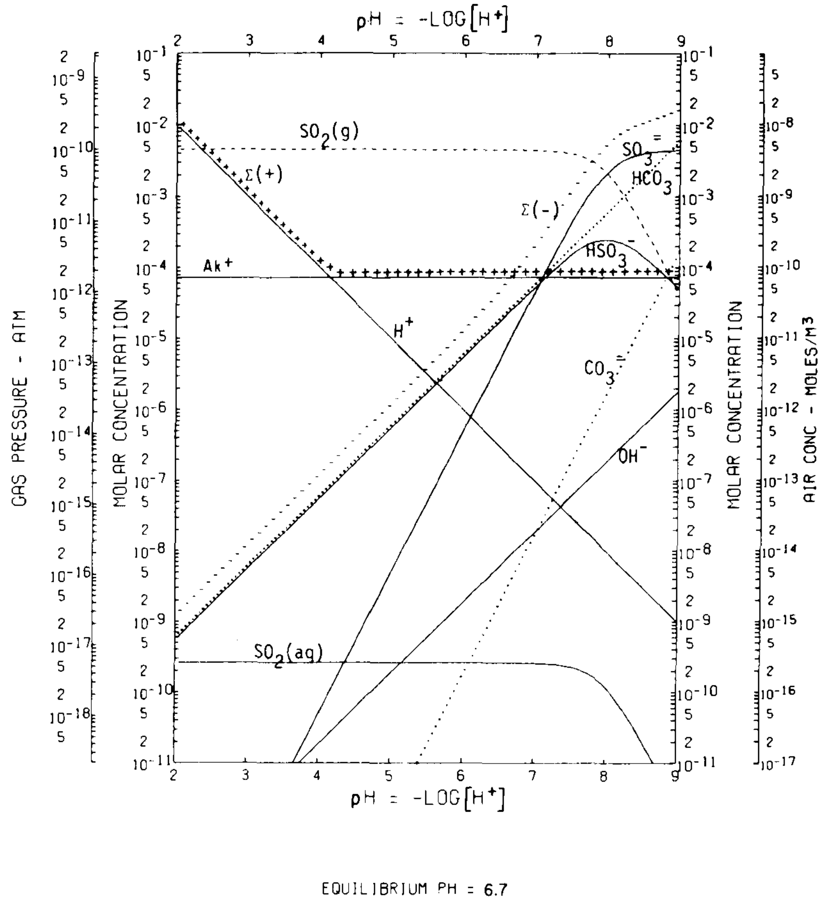

Fig. 5. Master variable diagram for the bulk sea-salt sample at 875 m altitude with input conditions: 0.0 $\mu g\ m^{-3}$ for sulfate ion and ammonium ion, 0.1 ppb sulfur IV (SO_2), 0.001 g m^{-3} liquid water, 340 ppm CO_2, and 278°K. Ak^+ refers to alkalinity.

cloud liquid water content as a function of height for each droplet size class, which allowed the total amount of water associated with both the sulfate and sea-salt droplets to be determined.

Specific chemical information from the master variable program is given in Tables 1, 2. In each case, the first column (A) applies to a small (dilute) droplet, the second (B) to the volume-weighted mean concentration of all sulfate or all sea-salt droplets, and the third (C) to a large (concentrated) droplet. The largest salt droplet carried in the growth calculations has a 32 μm radius and a sedimentation rate of about 0.13 m s^{-1}. Larger salt droplets will have fall speeds greater than the parcel updraft velocity and will be removed from the parcel. The sizes of droplets in the categories chosen are listed in the tables and their corresponding letter code is marked on the plots in Figs. 2, 3. Actual master variable diagrams for the volume-weighted mean cases are shown in Figs. 4, 5.

It is immediately evident that the compositions of the large and small droplets are substantially different not only from each other, but also from the volume-weighted mean. The pH ranges from 5.3 for the dilute sulfate droplets to 2.5 for the large concentrated ones, and from 5.5 for the dilute sea-salt droplets to 7.3 for the large concentrated ones. (The largest droplets are sufficiently concentrated for the alkalinity of sea-salt to influence the pH). Different ions control the equilibrium for the various sizes, with bisulfite and sulfite actually becoming important at the high pHs present in the large and bulk sea-salt categories. Such a range of chemical concentrations and compositions would validate the concerns of Perdue and Beck (1988), who pointed out that the bulk sample initially generated by mixing droplets of different pHs is not in equilibrium with the original in-cloud environment, and thus calculations of in-cloud SO_2 partial pressures from bulk water pH and sulfur (IV) concentrations may be in error.

Aqueous phase sulfate production is thought to occur when sulfur (IV) species (aqueous SO_2, bisulfite, and sulfite) are available for oxidation by hydrogen peroxide and/or ozone (Penkett et al., 1979; Hough, 1987), both of which are present in some marine environments at detectable levels (Barth et al., 1989). In the sulfate droplets, S(IV) is present primarily as bisulfite ion, and this ranges from 1.2×10^{-6} M in the small droplets to 2.0×10^{-9} M in the large ones. Hence, one would expect more sulfate production (per unit droplet mass) to occur in the small sulfate droplets. S(IV) in the bulk sea-salt sample (as bisulfite and sulfite) is 3.5×10^{-5} M in comparison to 3×10^{-7} M (as bisulfite) in the bulk sulfate sample. When the number of moles of S(IV) in all droplet size classes of each droplet type are added, the result is 7.2×10^{-11} moles kg^{-1} air for the sulfate droplets and 2.9×10^{-11} moles kg^{-1} air for the sea-salt droplets. The interesting conclusion is that although the mass of liquid water in sea-salt droplets is only about 1% of that in sulfate droplets (Tables 1, 2), 29% of the condensed phase S(IV) is contained in the relatively basic sea-salt droplets. These results confirm and supplement those of Hegg and Hobbs (1979), suggesting that in the early stages of cloud development, sulfate production will be a strong function of droplet composition and size. This dependence will not be incorporated into models which utilize only the bulk chemical composition.

4. Comparison with experimental results

Experiments in stratocumulus clouds in Sweden with a counterflow virtual impactor (CVI) which separates cloud droplets by size indicate that for droplets (of sizes between 4 and 12 μm radius) there is a systematic variation of concentration with size (Ogren et al., 1989). In 6 out of 7 sampling episodes, the larger droplets were more concentrated than the smaller ones by a factor of between 2 and 3. Droplet categories sampled by this instrument were much broader than those resolved by our model, and thus the differences in measured concentrations between the broader size categories would be expected to be much smaller than between the individual narrow size categories in this model.

In order to examine the results of our model for a range of droplet sizes which realistically might be sampled by such a size-selective instrument, the difference in concentrations between two broad categories was calculated by summing the calculated liquid water and sulfate masses in droplets of several more narrow categories. These new broader categories were 4.4 μm to 6.6 μm radius and 6.7 to 8.5 μm radius, approximately matching cut sizes used in some CVI experiments, and representing the full distribution of activated sulfate droplets in the model at 875 meters altitude. The resulting sulfate concentration ratio of the large droplets to the smaller droplets was 9.8. The difference between this value and those measured experimentally is not surprising for the reasons given below.

First, the droplet population which resulted from the model was generated from a specific initial aerosol size distribution under a very controlled set of growth conditions (constant updraft, no entrainment, sedimentation, or coalescence) and was thus different in size and probably much narrower than the one observed in Sweden. Secondly, the droplet population in our model was nucleated on a simple marine aerosol and so was obviously different in composition than the continentally-influenced one in Sweden. Finally, the actual cut size of the cloud probe, as a virtual impactor, does not assume a single value, but a *range* of values with different collection efficiencies around the radius of 50% collection efficiency (Noone et al., 1988). This means that in Sweden, droplets in different size categories near the cut size of the probe were all sampled together, reducing the magnitude of difference in concentrations from the model calculations.

5. Conclusions

A simple adiabatic parcel model has shown that under diffusional growth conditions near the base of a clean marine cloud, a wide range of chemical compositions and concentrations should establish itself in droplets within a few tens of meters above cloud base. In the absence of entrainment, coalescence, or chemical reactions, the smaller droplets should be more dilute than the larger droplets due to their more rapid growth rate relative to their initial CCN size. Using chemical equilibrium calculations, the pH ranged from 2.5 to 5.3 for droplets nucleated on ammonium bisulfate and from 5.5 to 7.3 for the more alkaline droplets nucleated on sea-salt particles.

This size-dependent droplet chemistry should play an important role in determining where further chemical reactions will most likely take place. Aqueous phase sulfate production will tend to occur in droplets with high S(IV) levels, which in this case would be the smallest sulfate droplets and all the sea-salt droplets. Although they contained only about 1% of the liquid water, a substantial percentage of the total aqueous S(IV) in the cloud was present in the more basic sea-salt droplets.

The volume-weighted mean or bulk droplet composition of a cloud will not, in general, represent the composition of individual cloud droplets. In order to determine accurately the true distribution of chemical species in a cloud, both models and measurements should take this size-dependent chemistry into account.

6. Acknowledgements

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