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A cloud microphysics model including trace gas condensation and sulfate chemistry

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A one-dimensional model for simulating the evolution of physical and chemical properties of an aerosol population has been developed in order to simulate cloud or fog droplet formation. The physicochemical processes affecting the aerosol population and included in the model are condensation and evaporation of water vapor and trace gases, gas emissions, and reversible and irreversible chemical reactions producing sulfate in the liquid phase. The model also includes modules for equilibrating the aerosol population with water vapor and trace gases, and for calculating the optical properties of the aerosol population. In this article, we compare the model results with other cloud models, and show that very similar fractions of activated particles are obtained using the thermodynamical models EQUISOLV II and AIM. We point out that when ammonia and strong acids (nitric and/or hydrochloric) are present in the system, the methods for the initial equilibration of the semi-volatile compounds can have a significant effect on the simulation results. We also compare the effects of nitric and hydrochloric acid with cloud drop activation and study sulfate production in the presence and in the absence of condensable trace gases.

Introduction

The impact of aerosols on climate change has been widely recognized and is an active area of research. Aerosol particles affect the radiative balance of the Earth both directly by scattering sunlight back to the space and indirectly by acting as cloud condensation nuclei (CCN). The first indirect aerosol effect on climate — i.e. the increased brightness and lifetime of clouds caused by increased anthropogenic CCN concentrations — is the largest single source of uncertainty in the quantification of the climate change that has occurred since the pre-industrial times. Beside the indirect aerosol effect, there are chemical effects that may also change cloud properties (Charlson *et al.* 2001). These effects include the reduction of the surface tension of cloud droplets (Facchini *et al.* 1999), dissolution of material to cloud droplets from slightly soluble aerosol compounds (Shulman *et al.* 1996), and condensation of water-soluble trace gases into CCN which have not yet activated into cloud droplets (Kulmala *et al.* 1993, Laaksonen *et al.* 1998). We have constructed a cloud microphysics model with the purpose of parameterizing the soluble gas effect in such a way that its global influence can be studied in climate models. In this paper we present the new cloud model, verify its operation against earlier models, compare the model outcomes when two different subroutines are used to represent the aqueous phase thermodynamics, and present some new results on the influence of trace gases on cloud properties.

The thermodynamic properties of aqueous aerosol droplets have a significant effect on the formation and evolution of the cloud, since for example the condensation of gases onto the droplets depend on the difference between the partial pressures of gases on the droplet surface and the partial pressures of gases further from the droplets. Models that calculate the thermodynamic properties of aqueous solutions have evolved greatly during the last ten years and the species included in the models have increased. In our aerosol model we have applied the thermodynamic models EQUISOLV II (Jacobson 1999) and AIM (Clegg *et al.* 1998).

The model

Overview

The aerosol model is a moving sectional model in which the sections are defined using a constant volume ratio between adjacent sections. The model solves ordinary differential equations describing condensation, evaporation, chemical reactions in the liquid phase, adiabatic variables and the emissions of gas phase species. The differential equations are solved using ode-solver DLSODE, from the Netlib repository (www.netlib.org) which solves initial-value problems for stiff or non-stiff ordinary differential equations using backward differentiation formulas (BDF).

The liquid phase concentrations c (mol cm^{-3}-air) for species q for each size bin i are derived from differential equations

$$\left(\frac{dc_{q,i}}{dt}\right) = \left(\frac{dc_{q,i}}{dt}\right)_{\text{chem}} + \left(\frac{dc_{q,i}}{dt}\right)_{\text{cond}} + \left(\frac{dc_{q,i}}{dt}\right)_{\text{vol}} \tag{1}$$

The gas phase concentrations C_q (mol cm^{-3}-air) for each gas phase species q are derived from

$$\left(\frac{dC_q}{dt}\right) = \left(\frac{dC_q}{dt}\right)_{\text{cond}} + \left(\frac{dC_q}{dt}\right)_{\text{chem}} + \left(\frac{dC_q}{dt}\right)_{\text{emis}} + \left(\frac{dC_q}{dt}\right)_{\text{vol}} \tag{2}$$

In Eqs. 1 and 2, ‘cond’ = condensation and evaporation, ‘chem’ = chemical loss and production, ‘emis’ = emissions of gas phase species, and ‘vol’ = change in concentration due to adiabatic expansion of volume.

The adiabatic equations include differential equations for total pressure, air temperature and the altitude of the air parcel. The adiabatic equations solved with the model depend on the type of simulation. For cloud model simulations, the air parcel is assumed to have a constant vertical speed, and the total pressure and the air temperature are functions of vertical speed. If we make simulations for fog formation, the vertical speed is zero. Thus, the pressure remains constant, but a temperature profile as a function of time is given. A detailed description of the cloud microphysics model has been presented by Kokkola (2003).

Thermodynamics

The liquid phase equilibrium can be calculated with basically any thermodynamic model, which solves equilibrium equations for water, dissolved species, ions, and solid phases. In this work, we used two thermodynamic models, namely EQUISOLV II (Jacobson 1999) and the aerosol inorganics model (AIM) by Clegg *et al.* (1998). From the equilibrium solver we obtain the concentrations of gases at the droplet surface for calculations of condensation and evaporation.

A comparison of results calculated with the two different thermodynamics is also presented in this article.

The liquid phase equilibrium reactions are assumed to be instantaneous, and thus the liquid phase species are assumed to be in equilibrium throughout the simulations. Also, the liquid phase diffusion is neglected and the composition of the individual droplets is assumed uniform everywhere in the droplet.

Initial conditions

By default, the aerosol population is assumed to be in equilibrium with the gas phase at the beginning of the simulation. The dissolved gases, ions and solids are assumed to be in equilibrium in the liquid phase. The initial equilibrium situation for a closed system is calculated with the thermodynamic equilibrium model.

After the initial equilibration, changes in ambient temperature and/or pressure cause a non-equilibrium between the gas phase and the liquid phase, resulting in condensation of gases into the droplets or evaporation of gases from the droplets. At this point also the liquid phase chemistry starts.

Calculations

Cloud model comparison

The cloud microphysics model was verified by comparing its results with seven cloud microphysics models. The purpose of this was to see how the results given by the current model differ from the results given by alternative cloud models and to shortly discuss the differences between the methods used by the current model and the alternative models. The authors and the types of the models in the comparison are listed in Table 1.

The first and the most detailed comparison was made with a cloud microphysics model from here on referred to as ADIA (Kulmala *et al*. 1998). The multi-component condensation equations used in the ADIA model have been compared with binary condensation experiments of nitric acid and water vapors (Rudolf *et al*. 2001). The model calculations and experimental results agree with each other remarkably well. Thus, the ADIA model should be a valid model for the verification. The ADIA model does not include oxidation of sulfate, so the main purpose of this comparison was to verify the condensation scheme used in the current model and the resulting fraction of activated droplets at different conditions.

Another brief comparison was made using simulation results from a cloud microphysics model by O'Dowd *et al*. (2000). The model includes SO_2 oxidation scheme, so the comparison focused on the sulfate produced during cloud formation.

Kreidenweis *et al*. (2003) presented a comparison of several cloud models in which the effect of sulfate production on aerosol mass and size distributions was studied. Both bulk models and size-segregated models were used in the comparison presented by Kreidenweis *et al*. In the present comparison, only the results given by size-segregated models were used. The details of the properties and configurations of the models have been presented by Kreidenweis *et al*. (2003) so the models are only briefly introduced in Table 1. All these models include oxidation of SO_2 to S(VI) by O_3 and H_2O_2.

Table 1. Main characteristics of the models used in the model verification.

References	Model type	SO_2 oxidation
Kulmala *et al*. (1998)	moving sectional	no
O'Dowd *et al*. (2000)	moving sectional	yes
Feingold *et al*. (1998)	moving sectional	yes
Gong (2002)	Lagrangian, re-mapped to initial grid	yes
Jacobson (2002)	moving sectional	yes
Liu and Seidl (1998)	moving sectional	yes
Nenes *et al*. (2001)	moving sectional	yes

Comparison with ADIA

In the comparison between the current model and the ADIA model, the fraction of activated particles was calculated for an adiabatically rising air parcel at different conditions. The calculations were made by varying the temperature, gas phase concentration of the volatile compounds and the vertical velocity of the air parcel.

A bimodal size distribution of ammonium sulfate $(NH_4)_2SO_4$ was chosen for the model comparison. The parameters for the dry size distribution are given in Table 2. The comparisons were made with two initial temperatures, 273.15 K and 294.15 K, and two vertical velocities, 0.1 m s^{-1} and 1.0 m s^{-1}. The gas phase species were NH_3, HNO_3 and HCl. The gas phase concentrations of NH_3 and HNO_3, for the individual runs can be seen in Fig. 1. The gas phase concentration of HCl was 1 ppb in all the runs.

Figure 1 shows the fraction of activated particles at the end of the run for different vertical velocities, initial gas phase concentrations and temperatures. In the simulations with the current model (crosses), all the volatile species except water were initially in the gas phase. This was because the ADIA model equilibrates only water, so to be able to compare the condensation schemes of the two models in a meaningful way, the initial conditions had to be made similar for both models.

It can be seen that when there was no initial equilibration for the gas phase species, the results matched each other closely when the initial temperature was 294 K (Fig. 1). With this initial temperature, the largest difference between the activated fractions for the two models was 0.066. This difference corresponds to three more size bins being activated in the ADIA model.

When the initial temperature was 273 K, the difference between the two models became slightly greater. The largest difference between the activated fractions for the two models at this temperature was 0.17, which corresponds to four more size bins being activated in the ADIA model. Although the difference in activated size bins is increased just by one compared with the 294 K simulations, the difference in activated fractions was increased relatively more because of the fact that the smallest activated size bin has a large number concentration.

Comparison with cloud model by O'Dowd *et al.*

The model for the irreversible chemical reactions was verified by making a comparison with the model calculations of O'Dowd *et al.* (2000) for sulfate formation. The calculations were made for a unimodal aerosol population of ammonium sulfate particles. The cloud base was at 1000 m and the height of the cloud was 300 m. The aerosol population was equilibrated at 97.5% relative humidity, 50 m below the cloud base. The vertical velocity of the air parcel was 0.4 m s^{-1}. The parameters for the dry aerosol population were: mean radius 0.075 μm, standard deviation 1.4, number concentration (case A) 44 cm^{-3} and number concentration (case B) 158 cm^{-3}. The simulations were done for two different initial volume mixing ratios of SO_2 of 0.5 ppb and 1.5 ppb. The gas phase volume mixing ratios for the other trace species were, O_3 = 30 ppb, H_2O_2 = 1 ppb, NH_3 = 1 ppb.

In the simulations, the current model was set up using nine volume ratio size bins. The liquid

Table 2. Parameters for the size distribution and initial conditions in the model verification runs.

Aitken mode			Accumulation mode		
R_p (nm)	N (cm^{-3})	σ	R_p (nm)	N (cm^{-3})	σ
20	1000	1.5	100	400	1.7
Initial conditions:					
Relative humidity (%)			95		
Pressure (mbar)			913.25		
Height (m)			200		

and the gas phase concentrations of all the trace species were brought into equilibrium in the beginning of the simulation. The aerosol liquid water was equilibrated simultaneously.

Table 3 shows the amount of sulfate produced by the model of O'Dowd *et al.* (2000) and by the current model for four different simulations. In the cloud simulations, most of the sulfate was produced by ozone, and because the reaction mechanism of oxidation of SO_2 by ozone is very much dependent on the hydrogen concentration, changes in hydrogen concentration influence the sulfate production strongly. From these calculations, it can be seen that for the sulfate aerosol population, the results of the two models matched each other closely.

Comparison with results given by Kreidenweis *et al.*

In the comparison described in Kreidenweis *et al.* (2003), a log-normal unimodal size distribution of slightly acidic ammonium bisulfate particles was used. The geometric mean diameter was 80 nm, the geometric standard deviation was 2 and the total number concentration of the particles was 566 cm^{-3}. The dry particles were assumed internally mixed and their composition is given in Table 4. The gas phase compounds included in the simulations and their initial gas phase concentrations are also shown in Table 4.

The simulations were made for a rising air parcel which moves with a constant vertical velocity. The simulation was run until the air parcel reached the altitude of 1200 m above the cloud base. The total simulation time was thus 2596 s. The current model was set up for the simulations as described in the previous section except that 60 volume ratio size bins were used.

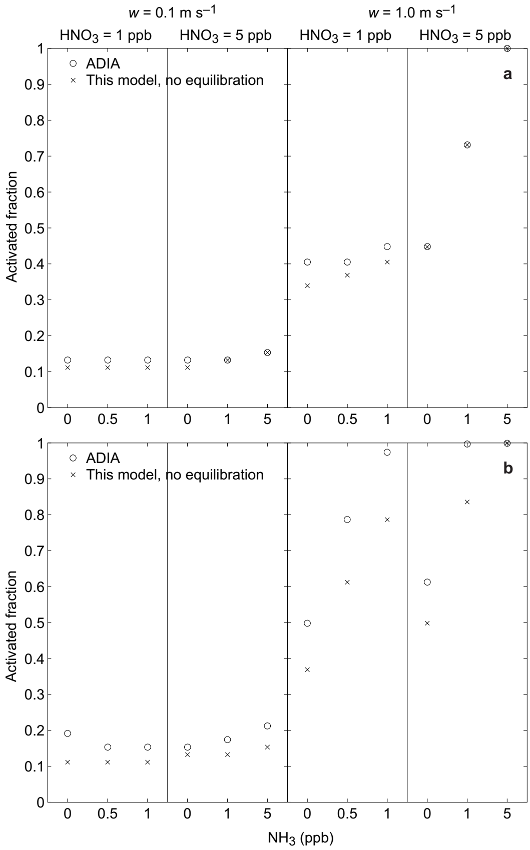

Fig. 1. Activated fraction calculated using the model ADIA and the current model without the initial equilibration at (**a**) T = 294 K and (**b**) T = 273 K.

The different models start calculation of the aqueous chemistry at different times. The model by Feingold *et al.* (1998) starts the aqueous chemistry when the ionic strength is less than 2 M and the model by Gong starts it at activation, while the other models calculate the aqueous chemistry from the beginning of the model run. In the current model, aqueous chemistry is also calculated from the beginning of the simulation.

Table 3. Sulfate formation for different initial concentrations of SO_2 and different size distributions.

Case	SO_2 (ppb)	Sulfate produced (µg m^{-3}) (O'Dowd *et al.*)	Sulfate produced (µg m^{-3}) (current model)
A	0.5	1.59	1.70
B	0.5	1.57	1.64
A	1.5	2.86	2.48
B	1.5	2.63	2.43

In the comparison with the results presented by Kreidenweis *et al*. (2003), the focus was on the sulfate production and the number of activated droplets calculated by the different models. Table 5 lists the results for the simulation. In the table, the number of activated droplets N_D, sulfate produced at the end of the simulation, and the maximum supersaturation during the simulation, are given.

It can be seen from Table 5 that especially the number concentrations of activated droplets differed significantly. The results given by the current model fell between the maximum and minimum values given by the other models. Still, the comparison shows that the results given by the current model are concurrent with the results given by the other models. The reasons for the differences in the results are numerous and they have been discussed by Kreidenweis *et al*. (2003).

Table 4. Initial conditions ($t = 0$).

Factor	Value
Height	600 m
Temperature	285.2 K
Relative humidity	95%
Pressure	950 mbar
Vertical velocity	0.5 m s^{-1}
Gas phase species	volume mixing ratio
SO_2	220 ppt
HNO_3	100 ppt
NH_3	100 ppt
H_2O_2	500 ppt
O_3	50 ppb
CO_2	360 ppm
Particle phase species	mass concentration
SO_4^{2-}	2 µg m^{-3}
NH_4^+	0.375 µg m^{-3}

The effect of the thermodynamic model

The current cloud model was also tested with the AIM model which uses the Pitzer, Simonson and Clegg method for calculating the activity coefficients and solves the thermodynamic equilibrium using iterative method for minimizing the Gibbs free energy. The results calculated using the AIM model and the EQUISOLV II were compared. The reasons for carrying out such a comparison are twofold. First, although both models converge toward the Debye-Hückel limiting law when the solutions are dilute enough (ionic strength below about 0.1 M), and activating droplets can have ionic strengths below 0.01 M at the maximum RH, it should be noted that the equilibrium curves do not solely determine the activated fraction of the droplet population. As shown by Nenes *et al.* (2001), also condensation kinetics influences the activation, and the equilibrium droplet composition before the saturation maximum certainly has an influence on the evolution of the droplet population. According to our model results, the droplets may be more concentrated than 0.1 M at the RH of 100%. Secondly, as shown below, the initial equilibration taking place at the RH below 100% can have a strong effect on the model results when semi-volatile species are present in the system.

The parameters for the simulations were equal to those used in the comparison with the ADIA model, except that HCl was not present in these simulations. The reason for omitting HCl was the fact that the AIM model is not valid for calculating thermodynamic equilibrium for a system which includes NH_4^+ and Cl^- ions concurrently. Also, in order to have a closer look at the temperature dependences of the two models, one set of simulations was calculated at cooler conditions with an initial temperature of 253 K.

Table 5. The models used in the comparison, and the calculated number of activated droplets N_D, produced sulfate during a cloud simulation, and the maximum supersaturation S_{max} calculated using the models.

References	N_D	Sulfate produced	S_{max}
current model	289 cm^{-3}	176.31 ppt	0.257%
Feingold *et al*. (1998)	310 cm^{-3}	169.59 ppt	0.368%
Gong (2002)	283 cm^{-3}	179.80 ppt	
Jacobson (2002)	275 cm^{-3}	169.10 ppt	0.257%
Liu and Seidl (1998)	358 cm^{-3}	176.93 ppt	0.248%
Nenes *et al*. (2001)	301 cm^{-3}	170.00 ppt	0.235%

A more detailed review of different inorganic aerosol thermodynamic equilibrium modules was presented by Zhang *et al*. (2000), so here the emphasis is on the differences on the results of cloud model simulations made with the two different thermodynamic models.

Figure 2 shows the results of simulations using two different thermodynamic models, EQUISOLV II and AIM. Altogether, twelve combinations of different temperature, vertical velocity and the initial gas phase concentration of NH_3 and HNO_3 are shown. It can be seen that the simulations with the two thermodynamic models give very closely matching results. The biggest difference between the activated fractions was for the case where the vertical velocity was 1 m s^{-1} and initial volume mixing ratios were 1 ppb for HNO_3 and 0.5 ppb for NH_3. In this simulation the difference between the activated fractions was 0.0537, which corresponds to a difference of two more size bin activated using the AIM model. In all the runs the difference was maximally two size bins. The differences in results using the two different thermodynamic models increased with a decreasing temperature. This is probably caused by the different methods for calculating the activity coefficients. Although the parameterizations of the two models are the same, EQUISOLV II uses mixed activity coefficients, whereas AIM uses single-ion activity coefficients for the mixtures.

Comparison between HNO_3 and HCl

In the past, Kulmala *et al*. (1998) noted that nitric and hydrochloric acids have quite similar effects on cloud drop activation, but no quantitative results were presented. We, therefore, compared the effects of HNO_3 and HCl on cloud drop populations.

The calculations were made using two particle populations: sodium chloride and ammonium bisulfate particles. The size distribution for sodium chloride particles was defined using the parameters shown in Table 1. The initial temperature was 273 K, initial RH was 90% and the vertical velocity was 0.5 m s^{-1}. Concentrations of gas phase species were 0–0.5 ppb for NH_3, 0–1 ppb for HNO_3 and 0–1 ppb for HCl, such that the sum of the acids was 1 ppb. Both types of initial situations, equilibrated and non-equilibrated with respect to the volatile species, were tested.

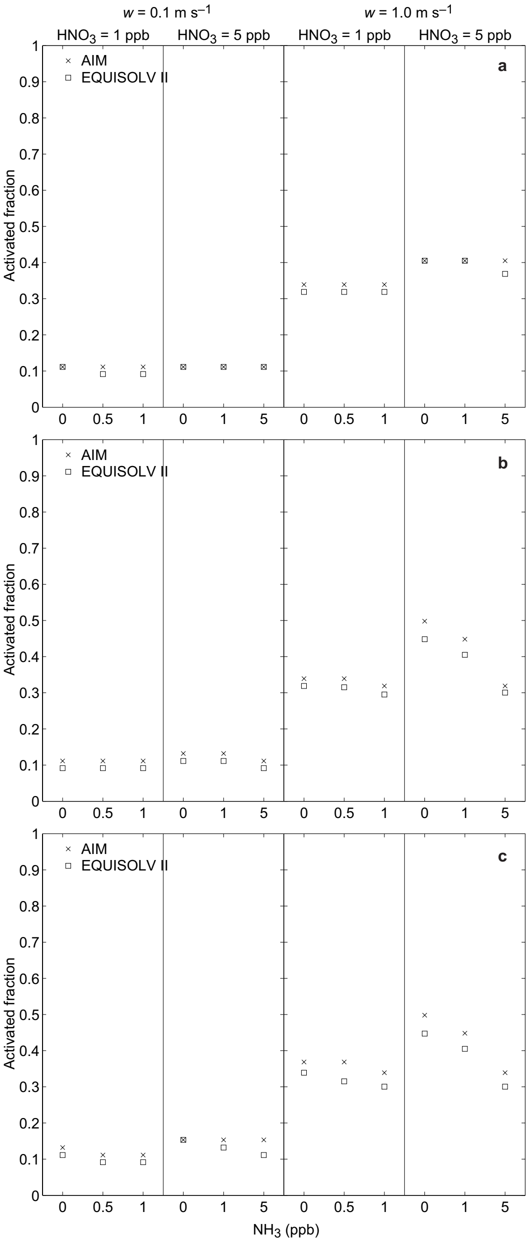

Fig. 2. Activated fraction calculated using the current model using two different thermodynamical models at three for initial temperatures (**a**) T = 294 K, (**b**) T = 273 K, and (**c**) T = 253 K.

The calculations for ammonium bisulfate particles were made using the size distribution also used in the comparison with results given

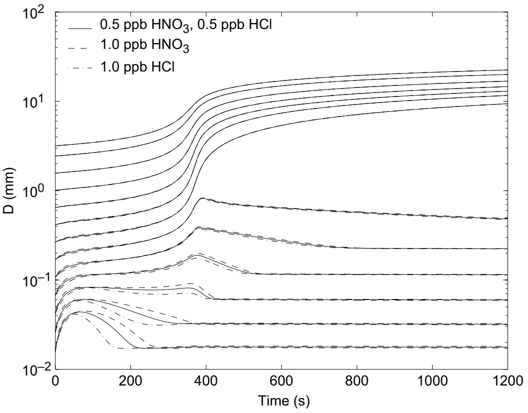

Fig. 3. Radius of the different size bins as a function of time for three different combinations of initial gas phase concentrations of HNO_3 and HCl: HNO_3 = 0 ppb and HCl = 1 ppb (run 1), HNO_3 = 0.5 ppb and HCl = 0.5 ppb (run 2), and HNO_3 = 0.5 ppb and HCl = 0 ppb (run 3).

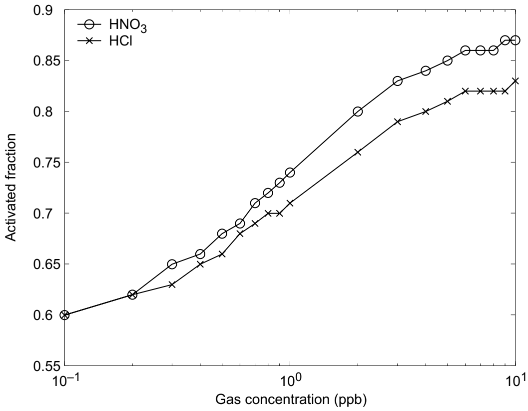

Fig. 4. Activated fraction as a function of initial gas phase volume mixing ratio of HNO_3 (circles) and HCl (crosses).

by Kreidenweis *et al*. (2003). The initial temperature was 273 K, initial RH was 90% and the vertical velocity was 0.5 m s^{-1}. The gas phase concentrations of HNO_3 and HCl were varied between 0.1–10 ppb.

Figure 3 shows growth curves at three different gas phase concentrations when there was no equilibration in the beginning of run. It can be seen that at low trace gas concentrations, the curves for different simulations were very similar, almost overlapping with each other. With initial equilibration of the gases the curves were even closer to each other. From Fig. 4 we can see that at higher concentrations small differences appeared, with HNO_3 increasing the activated fraction somewhat more compared with HCl. The differences in the activated fraction were caused mainly by different diffusion coefficients. The diffusion coefficient is larger for smaller molecules, and therefore D_{HCl} was smaller than D_{HNO3}. A large diffusion coefficient enhances the gas-liquid mass flux, causing big droplets to be closer to equilibrium. Also, an acid having a larger diffusion coefficient is depleted more rapidly from the gas phase. On the other hand, an acid with a smaller diffusion coefficient is collected efficiently by droplets close to the critical size, which causes enhancement of the activated fraction. Also, the thermodynamical properties of HNO_3 and HCl are different. The effective Henry's law constant for HNO_3 is higher than for HCl and this increases the number of activated droplets.

Differences also arose when the gas phase concentrations were compared as a function of time. Figure 5 shows two situations: (a) equal amounts of NH_3, HNO_3 and HCl in the gas phase and (b) more HNO_3 and HCl than NH_3 in the gas phase. It can be seen that HCl persisted longer in the gas phase than HNO_3. In more acidic conditions this behavior was stronger, as the condensation of nitric acid caused hydrochloric acid to evaporate temporarily out of the liquid phase (grey lines in Fig. 5). This phenomenon of NO_3^- driving Cl^- out of the droplets has been observed also in previous studies (Meng and Seinfeld 1996).

The role of initial equilibration

By default, all the semivolatile species are equilibrated in the beginning of the simulations in the current model. By contrast, the ADIA model and the models by Feingold *et al*. (1998), Gong (2002), and Nenes *et al*. (2001) do not equilibrate semivolatile species in the beginning of the simulation. The model by Liu and Seidl (1998) equilibrates NH_3 and in the model by Jacobson (2002) initial equilibration can be done, but in the simulations discussed by Kreidenweis *et al.* (2003) the Jacobson (2002) model was mostly run without initial equilibration.

To find out the effect of the equilibration on the results, simulations similar to those made

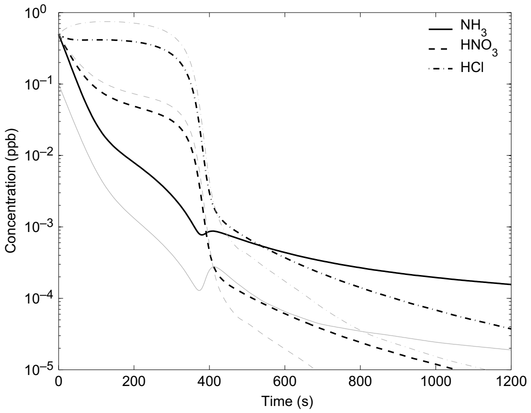

Fig. 5. Gas phase concentrations as a function of time, for two different runs with different initial NH_3 concentrations. Black lines correspond to initial situation with 0.5 ppb NH_3, HNO_3 and HCl. Grey lines correspond to initial situation with 0.1 ppb NH_3 and 0.5 ppb HNO_3 and HCl.

earlier were repeated using the initial equilibration option (Fig. 6). The simulations using the ADIA model are the same as those depicted in Fig. 1, but are included in Fig. 6 to visualize the comparison between the two models.

In these simulations, the differences between the ADIA model and the current model became much larger. Especially, when the initial concentrations of gaseous nitric acid and ammonia and the vertical velocity were high, the difference between the activated fraction was large. The largest differences occurred in simulations in which the vertical velocity was 1.0 m s^{-1} and the initial volume mixing ratio of both HNO_3 and NH_3 were 5 ppb. The difference between the activated fractions for these conditions at initial temperature of 273 K was 0.55. In the non-equilibrated simulations, both with ADIA and the current model, all 78 size bins were activated, but with initial equilibration, just 49 size bins were activated, corresponding to an activated fraction of 0.45. This is a large difference, and shows that especially when the concentrations are high, the initial equilibration of trace gases has a significant effect on the results of cloud simulations.

The reason for the differences in the results is that when there is no initial equilibration, a strong diffusive flux of the semi-volatile gases toward the droplets develops in the beginning of the simulation, resulting in a faster build-up of

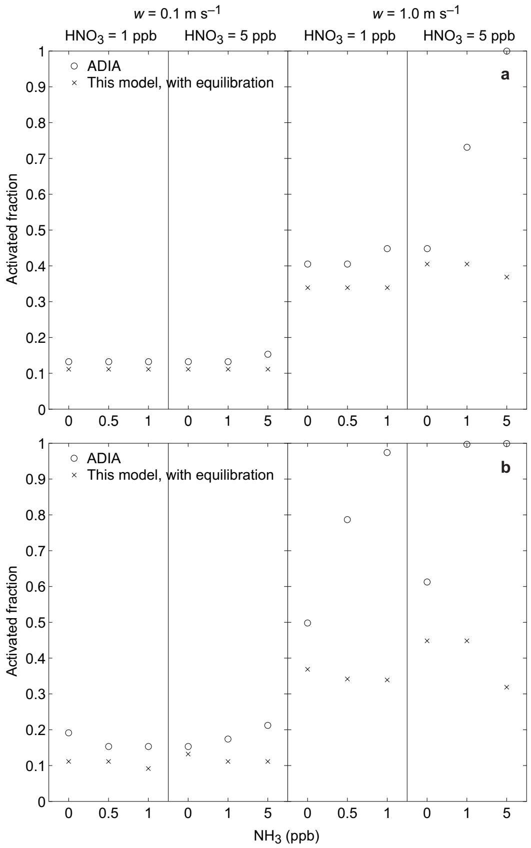

Fig. 6. The activated fraction of the droplet population in the end of the run calculated with ADIA without initial equilibration and the current model with initial equilibration. Initial temperatures are (**a**) 273.15 K and (**b**) 294.15 K.

the concentration of semi-volatile species in the small droplets than in the large droplets. This is due to the higher surface area to volume ratio of the smallest droplets. On the other hand, when the gases are equilibrated, the smaller Kelvin effect of the large droplets causes the concentration of the semi-volatile species to be higher in the large droplets. The difference in the size segregated partitioning of the trace species in the two cases thus causes the size distributions to be significantly different. In the simulations with initial equilibration, the size distribution is wider than in the non-equilibrated simulations.

The effect of the initial equilibration can be seen by plotting the evolution of the size distribution calculated with and without the equilibration. As an example, the case in which the equilibrated and non-equilibrated simula-

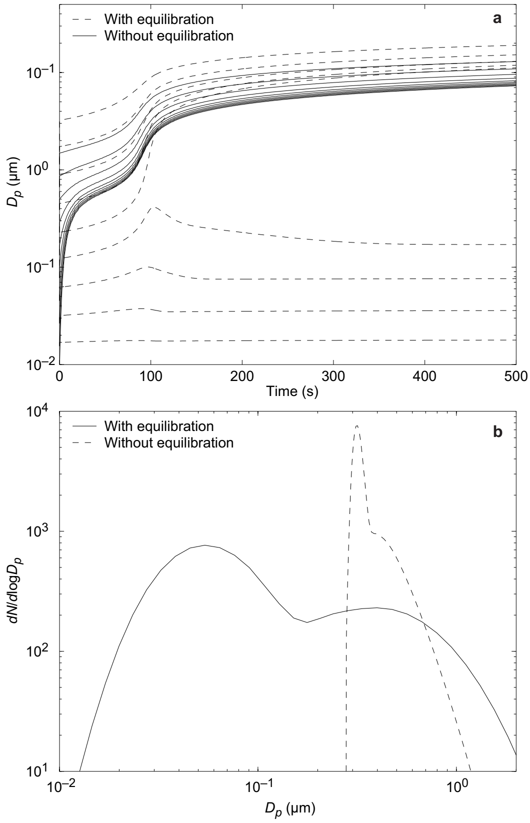

Fig. 7. — **a**: The radius of the size bins as a function of time with and without initial equilibration. — **b**: The size distribution at 15 s from the start with and without initial equilibration.

tions gave the biggest difference in the activated fraction was examined in more detail. Figure 7a shows how the radius of the particle changed in the two simulations. The dashed lines are for the case in which the semi-volatile gases were equilibrated at the beginning of the simulation and the solid lines are for the non-equilibrated case. Both simulations were carried out with the current model.

It can be seen that the initial size distribution was much wider when the initial equilibration had been made (Fig. 7a). Also, as the simulation started the size distribution sustained its shape, whereas the size distribution of the non-equilibrated droplet population changed significantly during the first seconds of the simulation. The volatile gases HNO_3, NH_3 and HCl condensed rapidly onto small droplets increasing their hygroscopic mass and thus increasing the condensation of water onto these droplets. Figure 7b shows the number size distribution 15 seconds from the start of the simulation for the equilibrated (dashed line) and non-equilibrated (solid line) cases. From this figure it can be seen how much narrower the size distribution of the non-equilibrated droplet became. In the non-equilibrated case, also the smallest particles grew large enough to reach the critical radius required for activation of the droplets and thus all the droplets were activated.

Time scales for the initial equilibration

To approximate the time scales which the system takes to reach equilibrium, model runs were carried out using a system with the same polydisperse particle population as used earlier in comparisons with the simulation by Kreidenweis *et al.* (2003), with 1 ppb of both HNO_3 and NH_3 initially in the gas phase. Only water was equilibrated in the beginning of the simulation. The particles consisted of 0.5 weight fraction of insoluble particulate matter and 0.5 weight percent of ammonium sulfate. The temperature was 273.15 K, pressure was 900 mbar, and relative humidity was 90%.

In order to see how the system approaches equilibrium, the environmental parameters were kept constant throughout the simulation. The semi-volatile species and water condensed into the droplets, thereby changing the size distribution as the condensing and evaporating nitric acid and ammonia adjusted the hygroscopic mass of the droplets. In Fig. 8, the solid lines show the development of particle diameters for the different sized bins. The crosses in Fig. 8 show the equilibrium sizes of the size bins for this system. It can be seen that, similarly to Fig. 7, a simultaneous condensation of nitric acid and ammonia in the small droplets rapidly increases their hygroscopic mass. At about one hour from the start, nitric acid began to leave small droplets and started to condense into larger droplets. The smallest droplets reached their equilibrium sizes at around one to two hours of the simulation time, whereas the largest droplets had not reached their equilibrium sizes even after 50 hours from the start of the simulation.

This test shows that the time scale for the largest particles to reach equilibrium is long compared with ambient atmospheric processes, for example temperature variations. On the other hand, the equilibration timescale of the smaller particles is on the order of an hour. This result is similar to that of Meng and Seinfeld (1996), who considered equilibration timescales of volatile species. For the smallest particles, the timescales of reaching equilibrium are on the same order as timescales for ambient temperature changes. Therefore, it is generally thought that the equilibrium assumption holds for particles smaller than roughly a micrometer which would support the initial equilibration of the trace gases in the beginning of a cloud model simulation as a more correct approach than partitioning the gases completely to the gas phase. However, this does not eliminate the fact that when condensable trace gases are present in the system, the equilibration RH strongly influences the activated fraction, and the proper choice of this RH probably depends quite much on the cloud type considered (e.g. convective *vs.* stratus clouds).

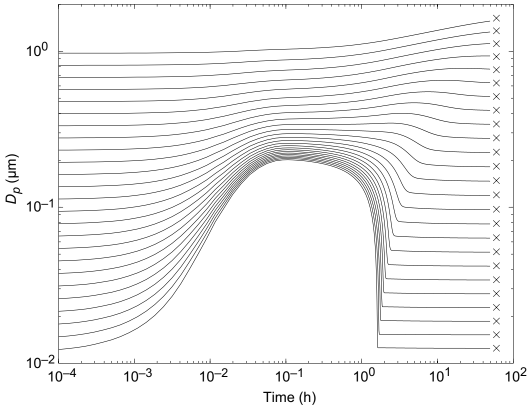

Fig. 8. Development of a size distribution as a function of time for a simulation in which the volatile species are initially in the gas phase and start condensing in the aerosol droplets.

Conclusions

Comparisons of the present cloud model with the ADIA model (Kulmala *et al.* 1998) gave a good correlation between two models for similar runs, as the largest difference in the calculated fraction of activated droplets was only four size bins. The largest differences, seen at low temperatures, can be explained by differences in the liquid-phase thermodynamics subroutines of the two cloud models. The simulations made with sulfate oxidation included showed a consistency with the model results by O'Dowd *et al.* (2000) and those presented by Kreidenweis *et al.* (2003). When compared with the results given by Kreidenweis *et al.*, the results of the current model were between the extremes of the results given by the other models. Comparison of the results from the present cloud model using two different liquid-phase thermodynamic subroutines (EQUISOLV II and AIM) showed no significant differences in calculated activated fractions.

Quite significantly, it was shown that initial equilibration of the condensable trace gases can lead to a significantly smaller fraction of activated droplets compared with model runs without trace gas equilibration. The cloud model presented here will be used in developing parameterizations of the influence of trace gases on cloud activation. In this context, the question of how to treat the initial equilibration becomes important. The results from the present simulations show that the activated fraction of droplets can vary greatly depending on whether the initial equilibration of the trace gases is made at a low RH or at a RH near 100%. Often, the cloud simulations are initialized at an RH greater than 97% (Hegg 2000, O'Dowd *et al.* 2000). To obtain realistic results, it has to be considered carefully whether the system can be in equilibrium at such a high relative humidity. An equilibrated system is generally thought to be closer to atmospheric conditions as compared with a non-equilibrated system. In reality, however, the whole droplet population is not necessarily in equilibrium because if the semi-volatile species are transferred into the droplets kinetically, the mass transfer will favor smaller droplets.

We also showed that HCl and HNO_3 cause a very similar increase in the activated fraction of cloud droplets at low and moderate gas phase concentrations. However, at higher gas phase concentrations HNO_3 increases the number of activated particles somewhat more, mostly due to its smaller diffusion coefficient.

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