

MODELLING FORMATION AND GROWTH OF H₂SO₄-H₂O AEROSOLS: UNCERTAINTY ANALYSIS AND EXPERIMENTAL EVALUATION

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Abstract—An aerosol dynamics model, AERO2, is presented, which describes the formation of H₂SO₄-H₂O aerosol in a smog chamber. The model is used to analyse how the uncertainties on four input parameters are propagated through an aerosol dynamics model. The input parameters are: the rate of the reaction between SO₂ and OH (k_1), the ratio between the nucleation rate used in AERO2 and that derived from classical nucleation theory (t_n), the H₂SO₄ mass accommodation coefficient (α) and a measure of the turbulence intensity in the reactor (k_c). Uncertainties for these parameters are taken from the literature. One of the results of the analysis is that AERO2 and aerosol dynamics models in general can only predict upper bounds for the total number (N_{tot}) and total volume (V_{tot}) concentrations of the particles. The uncertainties on N_{tot} and V_{tot} are mainly due to the uncertainties on k_1 and t_n . An uncertainty factor of 20–100 still remains when the uncertainty on k_1 is reduced to $\pm 5\%$. Aerosol measurements from three smog chamber experiments have therefore been used, in an attempt to reduce the uncertainty on k_1 and t_n . Values for k_1 are obtained in the reduced range 7.8×10^{-13} to 1.0×10^{-12} cm³ s⁻¹, which is within the range found in the literature. For t_n , values in the range 10^4 – 10^7 are obtained, which is close to the upper bound of the range in literature. These values for t_n are in marked contrast with a recent set of experiments on nucleation in H₂SO₄-H₂O mixtures, which suggests a value for t_n of at most 10^{-5} .

INTRODUCTION

Sulphate appears in atmospheric aerosol particles either through nucleation, or through condensation on pre-existing particles. Although the distinction between both processes is almost irrelevant in discussing the sulphate budget, it is of importance in considering some of the effects of the sulphate aerosol. Condensation does not increase the particle number concentration, however, it does change the chemical composition of the pre-existing aerosol, and hence its hygroscopic, optical and physical properties. Nucleation leads to the production of new particles, and it is the main mechanism of aerosol production in areas such as the remote marine troposphere or the stratosphere, where cloud formation requires such particles. Nucleation and condensation are furthermore coupled to the processes of coagulation, deposition and possibly others.

One of the first comprehensive models describing these dynamics and the resulting change in the aerosol size distribution dealt with the formation of H₂SO₄-H₂O particles from the gas phase (Middleton and Kiang, 1978). Since then many more models have been developed and applied to the H₂SO₄-H₂O system. Qualitatively, aerosol dynamics can be considered well understood at the present time. Examples of qualitative comparisons between model predictions and smog chamber experiments for the H₂SO₄-H₂O aerosol system are presented by McMurry (1980), Bunz and Dlugi (1991), Van Dingenen and Raes (1990a) and Lammel (1991). A quantitative validation of the models however is hampered by large uncertainties in some of the properties of the H₂SO₄-H₂O system and by the difficulty of determining experimentally all the parameters needed as input to the model.

In previous studies at our laboratory, we have attempted to reduce the uncertainty in a number of semi-empirical parameters related to the H₂SO₄-H₂O aerosol system, i.e. the turbulent deposition velocity of H₂SO₄ gas and particles (Van Dingenen *et al.*, 1989), the coagulation enhancement factor (Van Dingenen and Raes, 1990b) and the mass accommodation coefficient (Van Dingenen and Raes, 1991). This information has now been incorporated in the comprehensive aerosol model AERO2.

In the present study, a validation exercise has been conducted to ascertain the adequacy of AERO2 (and of any aerosol dynamical model in general) to make useful predictions about H₂SO₄-H₂O aerosol formation in a smog chamber. Both model prediction and experimental results are affected by uncertainty. As a result, the validation exercise requires the comparison between model and experiment over the entire space of the uncertainties. A three step procedure has been adopted. First, the uncertainty on the model output has been evaluated by propagating through the model the uncertainties on the input. Second, the model has been fitted to the results of three smog chamber experiments, using as adjustable parameters those that are indicated by the first analysis. Finally, the new values for the fitted input parameters are compared with the range of values in the literature.

THE MODEL

The model was named AERO2, with the 2 referring to the binary system that it describes. It was originally developed by Raes and Janssens (1986), and has since undergone extensive upgrading. The balance equations and numerical approach are outlined below. Subsequently, the aerosol physical input and its uncertainties are discussed.

Balance equations

A fair assumption in modelling the atmospheric H₂SO₄-H₂O system is that H₂SO₄-H₂O droplets are always in equilibrium with H₂O in the gas phase. The phase equilibrium is described by the generalized Kelvin equation

$$\ln \frac{S_A}{a_A} = \frac{2}{kT} \frac{M_A}{\rho} \frac{\sigma}{r} \left(1 + \frac{X}{\rho} \frac{d\rho}{dX} \right), \quad (1)$$

where S_A is the relative humidity, T the absolute temperature and r the radius of the droplet. The water activity a_A , the density ρ and the surface tension σ are functions of the weight % X of H₂SO₄ in the droplet. M_A is the mass of one molecule of H₂O and k is Boltzmann's constant. For a given temperature and relative humidity, equation (1) relates the number of H₂SO₄ molecules in the droplet (through X) to the radius. Hence, in describing the dynamics of a H₂SO₄-H₂O aerosol, either the number of H₂SO₄ molecules n in the droplet or the droplet radius r can be taken as the independent variable. Since book-keeping H₂SO₄ molecules during chemical reaction, nucleation, condensation and coagulation is more straightforward than following the particle radius, the first way is adopted in AERO2.

The evolution in time of the concentration of H₂SO₄ molecules in the gas phase [H₂SO₄^(g)] is given by

$$\frac{d[\text{H}_2\text{SO}_4^{(g)}]}{dt} = S - Ji^* - \sum_{i=i^*}^{\infty} C_i N_i - \lambda^{(g)} [\text{H}_2\text{SO}_4^{(g)}], \quad (2)$$

where S is the H₂SO₄ formation rate, J the nucleation rate, i^* the number of H₂SO₄ molecules in a critical cluster, C_i the collision frequency of H₂SO₄ molecules with a droplet containing i H₂SO₄ molecules, N_i the number concentration of droplets containing i H₂SO₄ molecules, $\lambda^{(g)}$ the deposition rate of H₂SO₄ molecules. The evolution of the particle concentration N_i is described by the following equations

$$\frac{dN_{i^*}}{dt} = J - C_{i^*} N_{i^*} - N_{i^*} \sum_{j=i^*}^{\infty} K_{i^*,j} N_j - \lambda^{i^*} N_{i^*} \quad \text{for } i=i^* \quad (3)$$

and

$$\begin{aligned} \frac{dN_i}{dt} = & C_{i-1} N_{i-1} - C_i N_i - N_i \sum_{j=i^*}^{\infty} (1 + \delta_{i,j}) K_{i,j} N_j \\ & + \sum_{j=i^*}^{i-i^*} \left(\frac{1 + \delta_{j,i-j}}{2} \right) K_{j,i-j} N_j N_{i-j} - \lambda^i N_i \quad \text{for } i=i^*+1, i^*+2, \dots, \end{aligned} \quad (4)$$

where $K_{i,j}$ is the coagulation coefficient for collisions between droplets containing i and j H₂SO₄ molecules, respectively, and λ^i the deposition rate for droplets.

Droplets with a diameter of 0.1 μm will contain several tens of thousands of H₂SO₄ molecules. In order to reduce the number of equations in equation (4), the size distribution is approximated by a sum of (up to) 70 monodisperse distributions, chosen at fixed particle diameters. This set of differential equations is solved using a 4th order Runge-Kutta procedure with variable time step (Raes and Janssens, 1986).

Aerosol physical input and discussion of uncertainties

H₂SO₄^(g) formation. In the atmosphere as well as in a smog chamber H₂SO₄^(g) is almost exclusively formed from the reaction with OH radicals, hence in equation (2)

$$S = k_1[\text{SO}_2][\text{OH}]. \quad (5)$$

In smog chambers, the concentration of SO₂ can be accurately measured. [OH] has either to be derived from a photochemical model or to be measured. Modelling may lead to an uncertainty up to 70% (Thompson and Stewart, 1991), while measuring realistic OH concentrations (i.e. around 10⁶ molecules cm⁻³) also leads to large uncertainties. However, even if [SO₂] and [OH] were accurately known, there would remain the uncertainty on k_1 , which, according to Atkinson *et al.* (1989), is of the order of a factor 2 ($\Delta \log(k_1) = +/ - 0.3$). Although the error in k_1 determined by a single laboratory is generally much lower, the factor of two accounts for interlaboratory differences.

Nucleation. Classical nucleation theory assumes a steady state distribution of H₂SO₄-H₂O clusters with sizes smaller than that of the critical cluster, and calculates the number of particles growing larger than this critical cluster per unit time. The most recent development of this concept is by Jaeger-Voirol and Mirabel (1988).

For what concerns the uncertainty related to the use of the classical nucleation theory, it is sufficient to know that the nucleation rate is critically dependent on the ratio $[\text{H}_2\text{SO}_4^{(g)}]/P_B^0(X)$, where $P_B^0(X)$ is the equilibrium vapour pressure of H₂SO₄ above a H₂SO₄-H₂O solution. $P_B^0(X)$ is derived from the H₂SO₄ activity coefficient $a_B(X)$, multiplied by the H₂SO₄ vapour pressure above a reference solution (i.e. a solution at which $a_B(X_{\text{ref}})$ is taken to be equal to 1). In the literature, there are two ways to calculate $a_B(X)$: Giauque *et al.* (1960) and Bolsaitis and Elliott (1990). Apart from defining different reference solutions, the latter also consider the presence of SO₃ above the H₂SO₄-H₂O solution. For determining the H₂SO₄ vapour pressure above the reference solution, use can be made of one of the three H₂SO₄ vapour pressure measurements reported in the literature. Of those, Ayers *et al.* (1980) give a range of uncertainty; from their equation (5), taken at 298 K and 100% H₂SO₄, P_B^0 is in the range 1.6×10^{11} – 1.3×10^{12} molecules per cm³. This range encompasses also the measurements of Roedel (1979) of Chu and Morrison (1980).

This 'choice' in selecting the thermodynamic data has a large effect on the nucleation rates. This is shown in Fig. 1, where the nucleation rate has been calculated as a function of the H₂SO₄^(g) concentration using the theory of Jaeger-Voirol and Mirabel (1988) and applying the possible range of thermodynamic data.

In the following AERO2 calculations, the nucleation rate obtained with $P_B^0 = 4.5 \times 10^{11}$ molecules cm⁻³ (Ayers *et al.*, average value) and the activities of Giauque *et al.* (1960) has been used as a reference. This rate is subsequently multiplied with a correction factor t_n . Figure 1 shows that due to the uncertainty in thermodynamic data alone, t_n is between 10³ and 10⁻⁷. Experiments by Wyslouzil *et al.* (1991), however, suggest values for t_n of at most 10⁻⁵ (see Fig. 1). This range of uncertainty of 10 orders of magnitude does not necessarily imply a similar range in the output of an aerosol dynamics model. However, even if we look at a more relevant parameter, namely the 'critical' H₂SO₄^(g) concentration at which $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$, the uncertainty spans nearly two orders of magnitude.

Condensation. Because the H₂SO₄-H₂O droplet is always in equilibrium with the H₂O vapour, the growth of the droplet is controlled by the collision of H₂SO₄ molecules and hydrates. The basic formula for the flux of H₂SO₄ molecules to a droplet with radius r_i ,

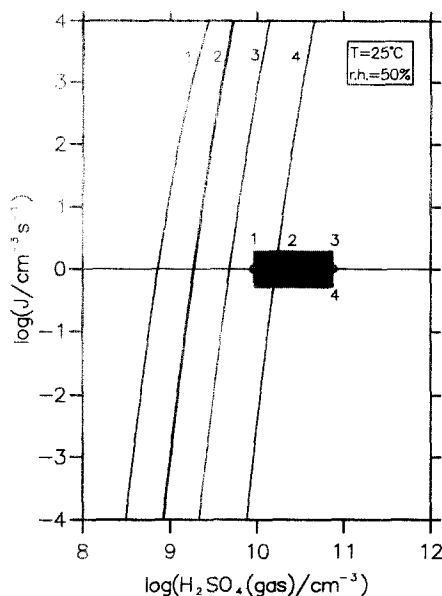


Fig. 1. Nucleation rates calculated with the theory of Jaeger-Voirol and Mirabel (1988), but using different thermodynamic input: (1), (2) and (3) are calculated, respectively, with Ayers *et al.*'s (1980) lower, average and upper value for the H_2SO_4 vapour pressure combined with Giaque *et al.*'s (1960) values for the H_2SO_4 activities, and (4) is with Ayers' upper value for the H_2SO_4 vapour pressure combined with the H_2SO_4 activities from Bolsaitis and Elliott (1991). The grey area bar shows the range of $\text{H}_2\text{SO}_4^{(g)}$ concentrations at which $J=1 \text{ cm}^{-3} \text{ s}^{-1}$, as extrapolated from the experiments of Wyslouzil *et al.* (1991). This range results again from the uncertainty in the H_2SO_4 vapour pressure, as indicated by the numbers.

covering both kinetic and diffusion regimes has been given by Fuchs (1934)

$$C_i = \frac{4\pi D r_i}{4D + \frac{r_i}{\alpha v r_i + r_i + \Delta}} ([\text{H}_2\text{SO}_4^{(g)}] - [\text{H}_2\text{SO}_4^{(g)}]^0), \quad (6)$$

where D is the diffusion coefficient of a H_2SO_4 molecule and v its mean thermal velocity. Δ is a distance from the particle surface, which artificially separates the kinetic from the diffusion domain. Δ has been taken equal to the mean free path length of the H_2SO_4 molecule. $[\text{H}_2\text{SO}_4^{(g)}]^0$ is the H_2SO_4 gas concentration in equilibrium with the droplet.

The accommodation coefficient α accounts for the fraction of H_2SO_4 molecules impinging on the droplet that effectively sticks to the droplet. α was experimentally determined by Van Dingenen and Raes (1991) who found a value between 0.02 and 0.09, at r.h. = 50% and aerosol diameters between 0.05 and 0.5 μm . The molar fraction of sulphuric acid in such particles is 0.12, for which Itoh (1990) calculated α to be 0.02, assuming Ayers *et al.* average value for P_B^∞ .

Equation (6) does not take into account the occurrence of H_2SO_4 hydrates. Relevant properties affected by hydrates are the diffusion coefficient D and the thermal velocity v . Van Dingenen and Raes (1991) re-analysed the condensation flux with these parameters weighted with the hydrate distribution prevailing at 50% r.h. The result is that the flux is lowered by less than 3%, which is a negligible change in view of the uncertainties on the accommodation coefficient.

Coagulation. The coagulation constant for collisions between droplets containing, respectively i and j H_2SO_4 molecules is given by (see Fuchs, 1964)

$$K_{i,j} = G(r_i r_j) \frac{16\pi \bar{D} \bar{r}}{\frac{4\bar{D}}{\bar{v} \bar{r}} + \frac{\bar{r}}{\bar{r} + \Delta}}. \quad (7)$$

This formula is similar to equation (6), in which $\bar{r}=(r_i+r_j)/2$, $\bar{D}=(D_i+D_j)/2$ and $\bar{v}=\sqrt{(v_i^2+v_j^2)}$. Δ' is taken as the average of the apparent mean free path length of the particles. $G(r_i, r_j)$ is a factor that accounts for the enhancement of the coagulation rate due to intermolecular (van der Waals) forces. Alam (1987) has calculated G for monodisperse salt particles ($G'(r)$) and Van Dingenen and Raes (1991b) have validated these calculations for H₂SO₄-H₂O droplets taking $G(r_i, r_j)=G'((r_i+r_j)/2)$.

Deposition. An expression for the deposition rate of particles and 'sticky' molecules on a reactor wall has been derived by Crump and Seinfeld (1981). The uncertainty in using this expression relates to the description of the turbulence in the reactor. This is done by introducing the eddy diffusion coefficient $D_e=k_e x^n$, where x is the distance from the wall and $n=2.6$, according to experiments by Okuyama *et al.* (1986) and Van Dingenen *et al.* (1989). In case of mechanically induced turbulence, the eddy diffusion parameter k_e can be calculated (Okuyama *et al.*, 1986). When turbulence is induced by convection, k_e can be determined by measuring the decay of a monodisperse aerosol in the vessel, and fitting the deposition rate expression to the observations. Our experience has shown that k_e can thus be determined within a factor 2 (Van Dingenen *et al.*, 1989)

ANALYSIS OF UNCERTAINTY PROPAGATION IN AERO2

Analysis technique and assumptions

As shown in the previous section the input parameters of the AERO2 model are affected by uncertainties of varying degrees. An attempt has been made to investigate how these uncertainties are propagated in the model results. Four input parameters have been taken as uncertain: the reaction constant k_1 , the nucleation correction factor t_n , the accommodation coefficient α and the intensity of turbulence k_e . The 'a priori' selection of these four parameters as being the most important is based on qualitative experience previously acquired with AERO2. The ranges of uncertainty attributed to each of these input parameters are given in Table 1, and are based on the discussion in the previous paragraph.

Using a straightforward Monte Carlo approach, values of these parameters have been sampled from assigned distributions that describe their uncertainty (see Table 1). AERO2 has then been run for 100 different combinations of sampled values to produce a histogram of the model output under consideration. Histograms have thus been generated for the number and volume concentration of the particles. The uncertainty associated with these output variables are studied by looking at their histogram's 25th, 50th (i.e. median) and 75th percentiles.

The next question is which of the input parameters is most responsible for the observed uncertainty on an output variable. This is studied by computing the latter's 'standardized

Table 1. Variable and fixed input data used for the uncertainty analysis of AERO2. For the variable input, the range of uncertainty is given, from which values are sampled each time a Monte Carlo run is performed. The sampled distribution is logarithmic (LOG) or linear (LIN)

Variable input	Range	Units	Sampling
Reaction constant SO ₂ +OH	k_1 4.5E - 13 - 2.4E - 12	cm ⁻³ s ⁻¹	LOG
Nucleation rate correction	t_n 1.0E - 07 - 1.0E + 03	—	LOG
Accommodation coefficient	α 0.02 - 0.09	—	LIN
Degree of turbulence	k_e 0.017 - 0.070	s ⁻¹	LOG
Fixed input			
Initial SO ₂ concentration	0.85	ppm	
OH time profile	As in experiment 2		
Temperature	25	°C	
Relative humidity	50	%	
Reactor radius	35	cm	

rank regression coefficients' (SRRC) with respect to the input parameters. Taking the particle number concentration N and the reaction constant k_1 as example of output and input variables, respectively, the value of SRRC (N, k_1) gives a measure of the influence of the uncertainty on k_1 on the uncertainty on N . SRRC's value ranges between -1 and $+1$; positive and negative SRRC values mean a positive and negative correlation between input and output, respectively. Absolute SRRC values close to unity indicate an influential parameter (as far as uncertainty propagation is concerned), whereas values close to zero indicate an irrelevant parameter. The analyses are performed by interfacing AERO2 with a general purpose Monte Carlo driver (Homma and Saltelli, 1991; Saltelli and Homma, 1991).

The uncertainty analysis of AERO2 presented here has been performed for the conditions of a well-defined set of experiments (see description below and Table 1). The initial SO_2 concentration, the OH profile vs time and the reactor geometry have been set to the values used in the experiments. The results of the uncertainty analysis are therefore only valid for conditions that resemble such laboratory conditions.

Results

The uncertainty propagation was studied with respect to the following output parameters: the total number and volume concentration ($N_{\text{tot}}, V_{\text{tot}}$) of particles as well as these concentrations as measured by a system with a lower detection limit of $0.017 \mu\text{m}$ ($N_{\text{meas}}, V_{\text{meas}}$).

Figures 2a and 2b show the median and 25 and 75 percentiles of N_{tot} and V_{tot} , resulting from the full uncertainties on all four input parameters given in Table 1. At any time point, the value distribution of N_{tot} and V_{tot} is very wide and asymmetric. As an example, the

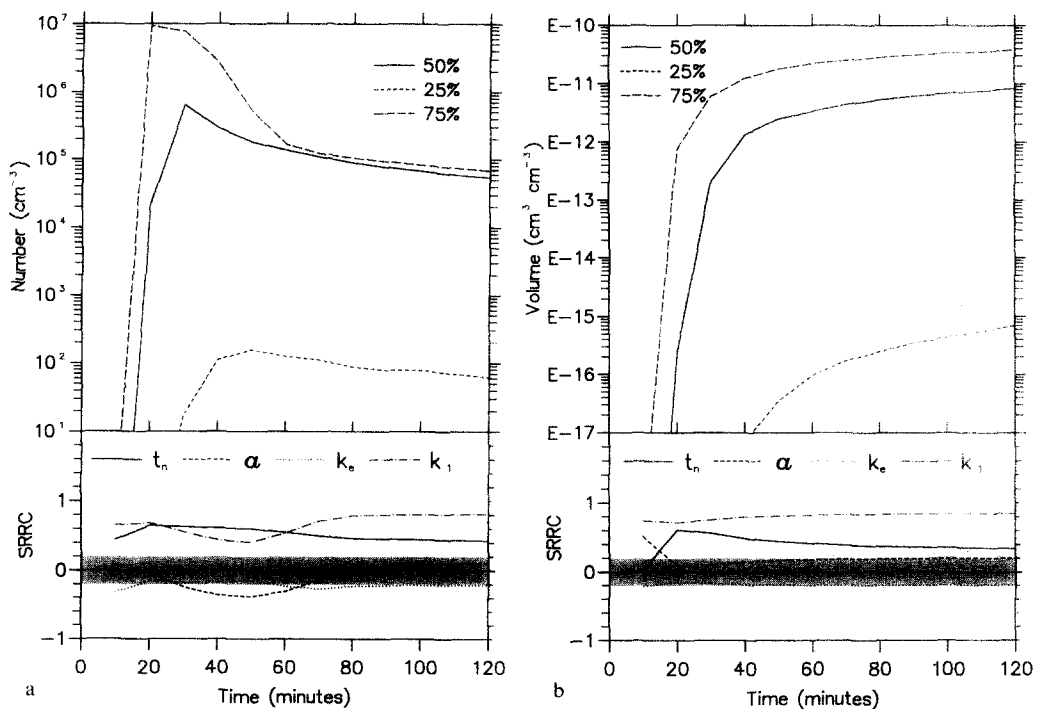


Fig. 2. (a) Median, 25 and 75 percentiles of the distribution of total number concentrations predicted by 100 Monte Carlo runs of AERO2. The uncertainties on the input parameters k_1 , t_n , α and k_e are given in Table 1. The absolute value of SRRC indicates the relative contribution of the uncertainty of each of the input parameters to the uncertainty on N_{tot} . The hatched area indicates a range close to zero where the contribution is less significant. (b) as in (a) but with respect to the total volume concentration.

histogram for N_{tot} at 30 min is shown in Fig. 3. It reflects the strong non-linearity of the nucleation process (see Fig. 1): small changes in the $[\text{H}_2\text{SO}_4^{(\text{g})}]$, caused by the random variability in the sampled input parameters, may determine whether there is particle formation or not. This results in output values between zero and some finite value. It must therefore be concluded that given the uncertainty on its input, AERO2 can only predict an upper bound for N_{tot} and V_{tot} .

The plot of the SRRC in Fig. 2a shows that the ranking of the input parameters with respect to their contribution to the uncertainty on N_{tot} changes during the course of the experiment. The total number of particles is positively correlated with t_n and k_1 . α contributes to N_{tot} in the period after the nucleation burst. The correlation between α and N_{tot} is negative, as a lowering of α increases $[\text{H}_2\text{SO}_4^{(\text{g})}]$, hence the nucleation rate, and hence N_{tot} . It might be wondered then why α is not significant earlier, around $t=20$ min, when nucleation is at its maximum. The explanation is that although α influences N_{tot} around this time point, its influence is small relative to the contributions of k_1 and t_n . The parameter k_e never significantly contributes to either N_{tot} or V_{tot} . This does not mean that deposition is an unimportant process, but that the range of uncertainty selected for this parameter is so narrow as to make variation within the range unimportant as far as N_{tot} and V_{tot} is concerned. The fact that t_n contributes to the error of N_{tot} and V_{tot} , even at 120 min, does not mean that nucleation occurs at 120 min, but reflects that despite coagulation, the values of N_{tot} and V_{tot} at 120 min are still determined by the strength of the nucleation burst around 20 min.

Figures 4a and b show the results of the analysis for N_{meas} and V_{meas} . The distribution of N_{meas} spans a shorter interval, due to the fact that, during the nucleation burst, most of the nucleation dynamics takes place below the assumed detection limit of the measuring instrument ($0.017 \mu\text{m}$). This also explains the reduced importance of t_n in the SRRC plot. At any time k_1 contributes most, and almost exclusively, to N_{meas} and V_{meas} . For the type of laboratory experiments discussed here, the uncertainty on α and k_e is negligible, compared with the uncertainties on the gas phase chemistry and nucleation rate. Note that α is now always positively correlated with N_{meas} . This reflects the fact that, in order to become detectable, the particles must first grow larger than the detection limit, and the easier they grow (i.e. α high), the more particles will be detected. Hence, even when a high α reduces new particle production (see Fig. 2a), the few that are formed are more easily detected.

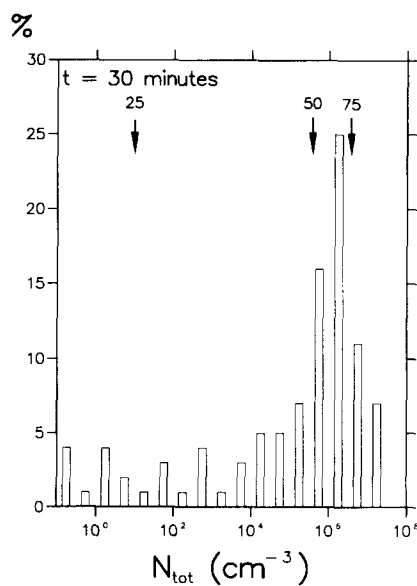


Fig. 3. Histogram of values of N_{tot} at $t=30$ min, generated by the same 100 runs of AERO2 as in Fig. 2a.

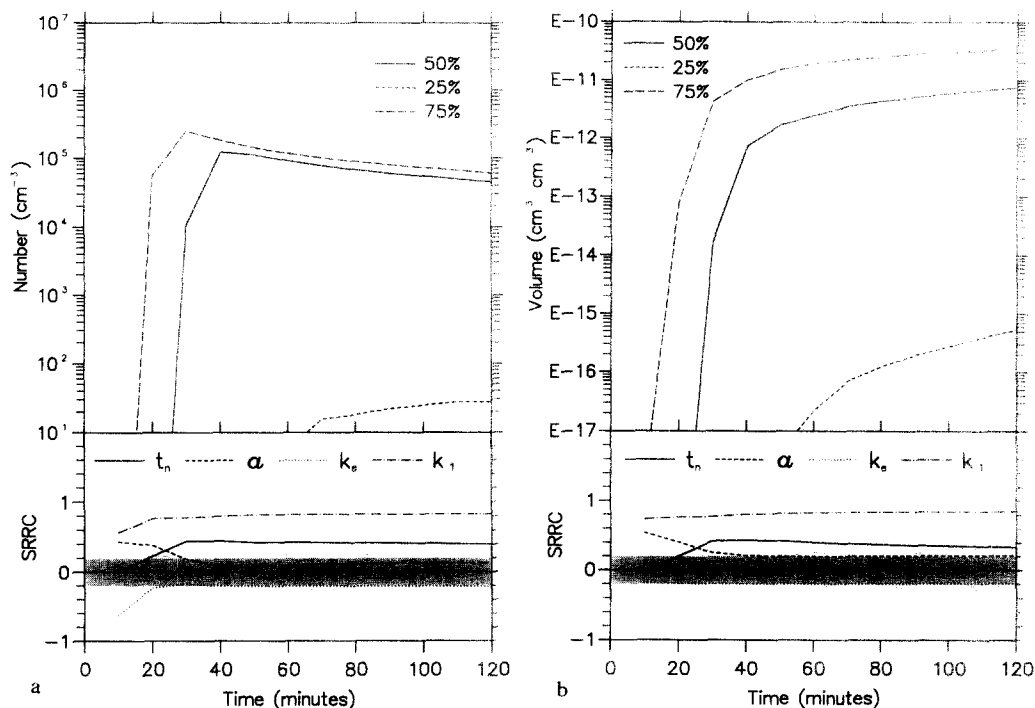


Fig. 4. As in Fig. 2 but with respect to the detectable fraction of the aerosol. A lower detection limit of $D_p = 0.017 \mu\text{m}$ is assumed.

The uncertainty on k_1 is a problem to be solved by gas phase chemists rather than by aerosol physicists. However, its predominant contribution to the uncertainty on N and V conceals the uncertainty propagation of the aerosol parameters t_n , α and k_e . A set of calculations is therefore performed in which it is assumed that k_1 is known within 10% ($1.0 \times 10^{-12} < k_1 < 1.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$), with the other uncertainties kept as in Table 1. Figures 5a and b show the results for N_{tot} and V_{tot} . In both cases, the overall uncertainty has been reduced, except during the nucleation burst, where N_{tot} is of the same order as in Fig. 2a. After the nucleation burst, a lower bound can now be predicted which is about 5% (for N_{tot}) and 1% (for V_{tot}) of the upper bound. For N_{tot} , the ranking of the uncertainties of the input parameters changes in the course of the experiment: t_n is always predominating, α becomes significant only immediately after the nucleation burst, whereas k_e becomes relevant only in the second half of the experiment. For V_{tot} the ranking is more constant throughout the experiment, with all three input parameters contributing significantly to the uncertainty.

UNCERTAINTY REDUCTION

It has been shown that the uncertainties in the model input parameters (see Table 1), propagate in such a way that only upper bounds for the aerosol number and volume concentrations can be predicted. When doing smog chamber experiments, however, it is certainly possible to observe in a reproducible way, whether or not particles are being formed, and number and volume concentrations can be measured with a greater accuracy than those indicated by the 25th and 75th percentiles resulting from the uncertainty analysis. It is therefore possible to set up smog chamber experiments to try to reduce the uncertainty in some of the input parameters. The SRRC plots in Fig. 4a and b, related to the measurable fraction of the aerosol, show that N_{meas} and V_{meas} are most sensitive to k_1 and t_n . It is therefore sensible to set up a series of chamber experiments to determine N_{meas} and V_{meas} and to determine k_1 and t_n by fitting AERO2 to these measurements.

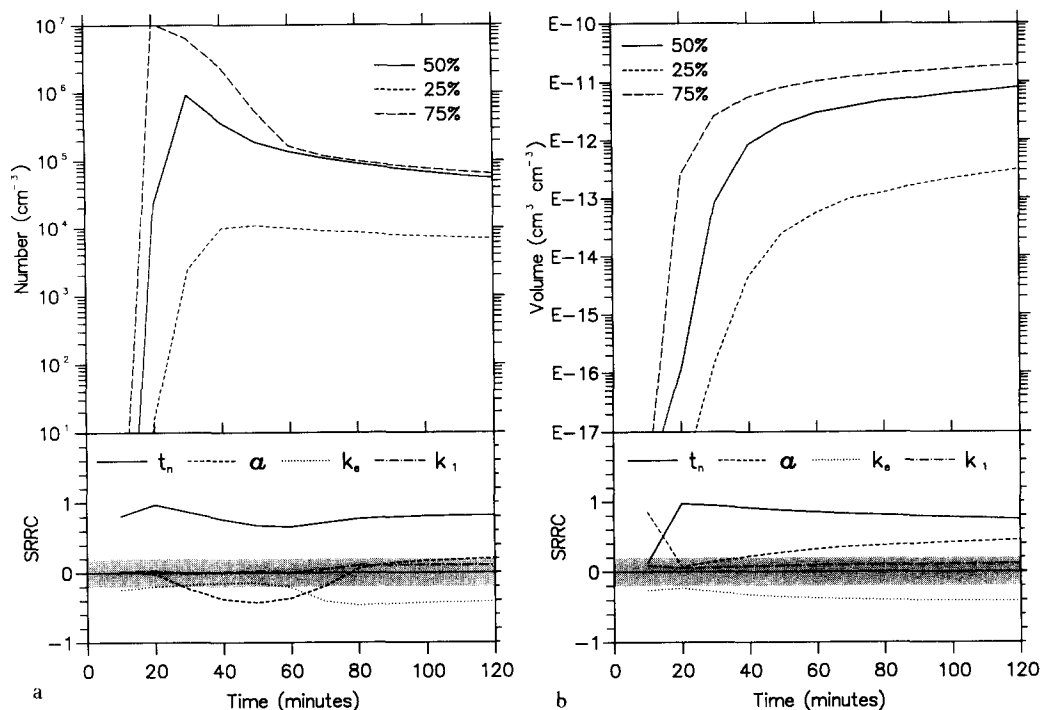


Fig. 5. As in Fig. 2, except for the uncertainty on k_1 which is set to 10% (1.0×10^{-12} – 1.1×10^{-12} cm³ s⁻¹).

Experimental set-up

A detailed description of the experimental set up and procedures has been given elsewhere (Van Dingenen and Raes, 1991). The H₂SO₄-H₂O aerosol is generated photochemically in a 230 l spherical batch reactor ($R = 35$ cm) made of glass. The turbulence in the reactor is generated by natural convection and is characterized by an eddy diffusion parameter $k_e = 0.035$ s⁻¹ ($\Delta \log(k_e) = \pm 0.3$). The reactor is filled initially with pure air and traces of SO₂ (870 ppbV), NO (540 ppbV), NO₂ (54 ppbV), propane (420 ppbV) and propene (420 ppbV). The temperature is 25 ± 1 °C, and the relative humidity 50%. HNO₂ is generated in the dark through heterogeneous reaction between NO_x, H₂O and the reactor wall. When the actinic lamps are switched on, OH radicals are formed that react with SO₂ and rapidly lead to the formation of an aerosol. During the course of the experiment, the size distribution of the aerosol is measured using a Differential Mobility Particle Sizer (TSI model 3932C-1) having a lower detection limit of $D_p = 0.017$ μm. At the end of the experiment the aerosol is sampled on a filter and analysed by ion chromatography.

According to the chemistry of the constituents of the mixture, only H₂SO₄ and HNO₃ are assumed to form as condensable products. Because of the relatively high vapour pressure of HNO₃, only H₂SO₄ and H₂O will nucleate to form particles. Furthermore, because of the high HNO₃ vapour pressure and because of the high acidity of the H₂SO₄-H₂O particles, HNO₃ will not condense on the particulate and will remain in the gas phase. This picture is corroborated by the ion chromatographic analysis, which reveals only the presence of sulphate and not of nitrate in the aerosol. Furthermore, taking the last DMPS measurement, and using equation (1), the H₂SO₄ content in the aerosol can be calculated yielding values within $\pm 20\%$ of the ion chromatographic measurement.

Analysis

Figures 6, 7 and 8 show the number and volume concentrations measured in three experiments. The fraction of the aerosol larger than 0.017 μm, the lower detection limit of

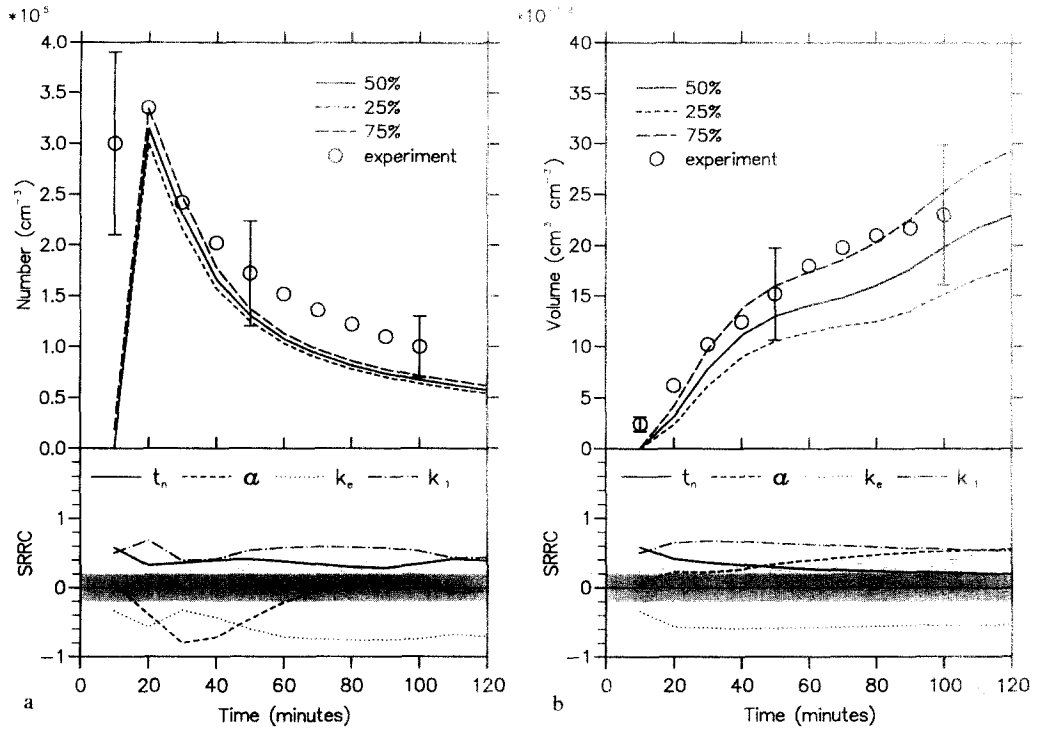


Fig. 6. Observed values of (a) N_{meas} and (b) V_{meas} and model simulations for experiment 1. The median, 25 and 75 percentiles are calculated after fitting of AERO2 to the three experiments, and taking the resulting range for k_1 (7.8×10^{-13} – $1.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) and for t_n (10^4 – 10^7) in the Monte Carlo simulation. The ranges for α and k_e are as in Table 1.

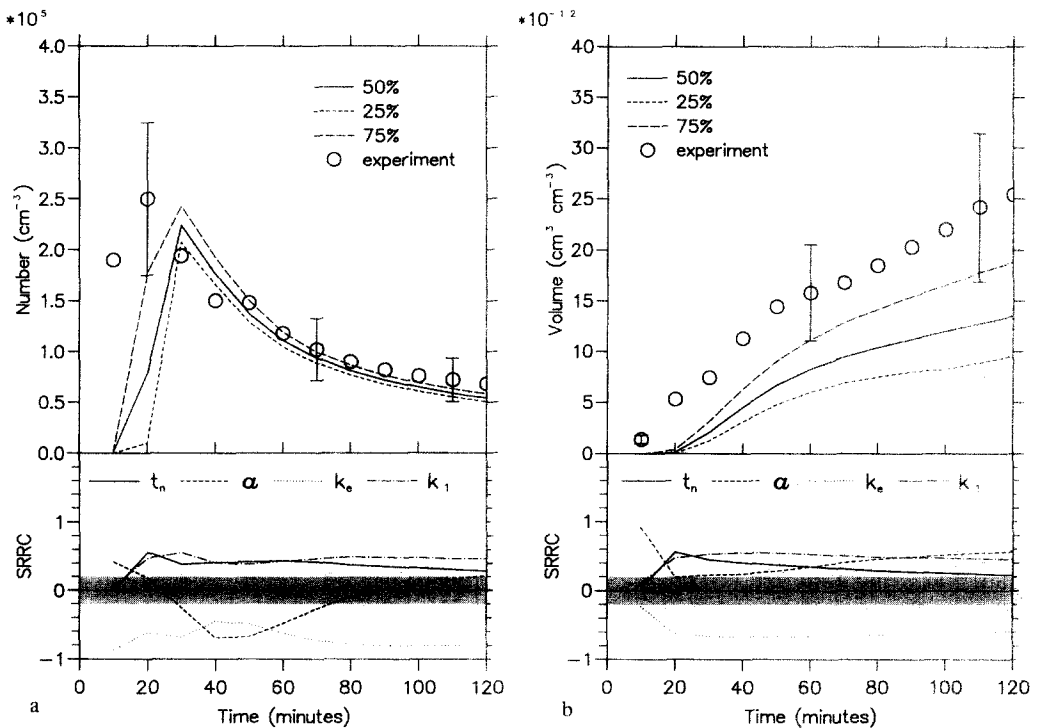


Fig. 7. As in Fig. 6, but for experiment 2.

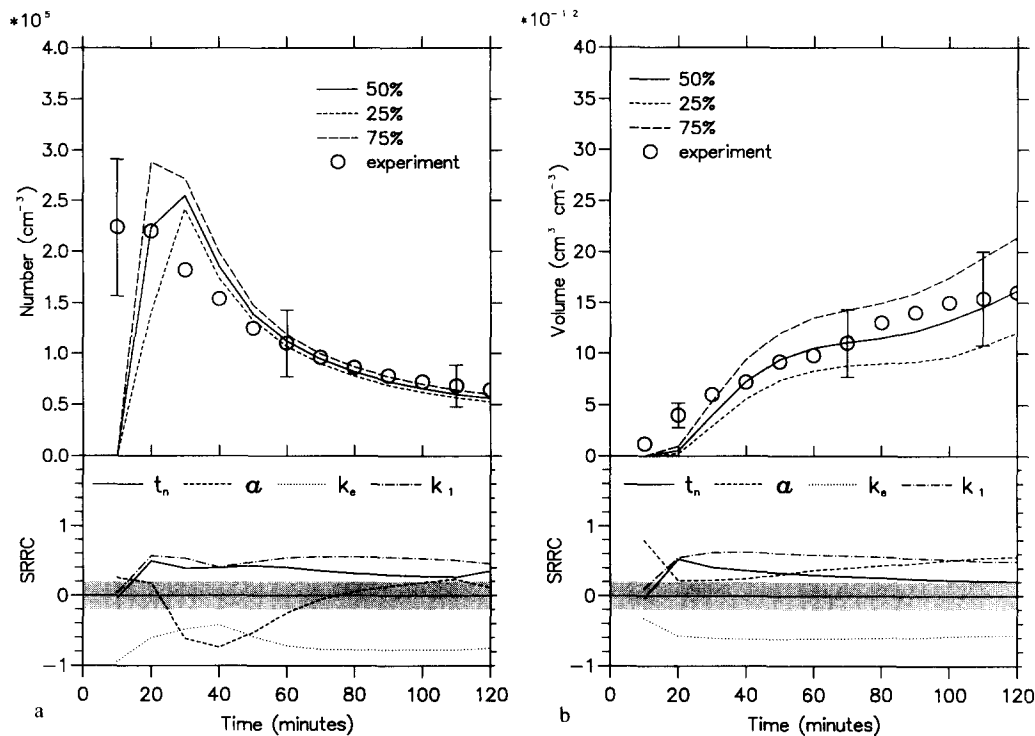


Fig. 8. As in Fig. 6, but for experiment 3.

the DMPS is shown. There are a number of reasons to believe that the values at $t < 30$ min are inaccurate: (1) only a fraction of the aerosol is larger than the detection limit at that time and (2) the DMPS, with its sampling time of 5 min cannot adequately follow the extremely rapid dynamics during nucleation, which typically leads to an overprediction of all aerosol parameters. These measurements will therefore be discarded in the following analysis, except for a single test calculation.

The SRRC plots in Fig. 4 showed that within the range of uncertainty of the input parameters, and for $t > 30$ min, N_{meas} and V_{meas} are sensitive only to k_1 and t_n . Hence, only the uncertainty on k_1 and t_n can be reduced using observations of N_{meas} and V_{meas} . AERO2 predictions have therefore been fitted to the experimental values of N_{meas} and V_{meas} . k_1 and t_n are taken as adjustable parameters without any constraints on the values they might be given in the fitting procedure, while α and k_e are kept fixed at 0.04 and 0.035 s^{-1} , respectively. The exact values of the latter parameters are not important as long as they are within the range given in Table 1.

The uncertainty on the observed N_{meas} and V_{meas} needed in the fitting procedure, is taken to be $\pm 30\%$. The best fit values for k_1 and t_n , for each of the experiments are given in Table 2, together with their standard deviation and the goodness of fit. It is shown that good fits are obtained returning rather accurate values for k_1 , whereas the values for t_n remain uncertain. From these three experiments, it is concluded that the value of k_1 is in the range 7.8×10^{-13} to $1.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The nucleation correction factor t_n will be much larger than 1 and without consideration of the standard deviations in Table 2 a range between 10^4 and 10^7 is obtained. As a test of the robustness of the above analysis a fitting of AERO2 to the observed N_{meas} and V_{meas} has been made, including the values at $t = 20$ min. It results that the range of k_1 remains unaffected, whereas t_n goes to even higher values.

Discussion

The range of values obtained for the reaction constant k_1 is within the range of uncertainty Table 1. This result, together with the agreement between the aerosol volume

Table 2. Best fit values for the $\text{SO}_2 + \text{OH}$ reaction constant (k_1) and the nucleation correction factor t_n , after fitting AERO2 simultaneously to the number and volume concentrations observed three smog chamber experiments

Experiment	k_1 ($\text{cm}^{-3} \text{s}^{-1}$)	$\sigma(k_1)$ (%)	t_n (—)	$\sigma(t_n)$ (%)	Goodness of fit
1	1.0×10^{-12}	36	10^4	35	0.99
2	9.4×10^{-13}	35	10^7	66	0.87
3	7.8×10^{-13}	50	10^6	93	0.99

measurements and the sulphate determinations reinforce the assumption that in the experiments described here, the reaction between SO_2 and OH eventually leads to an $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ aerosol. The fact that the range obtained is smaller than that in Table 1 shows that smog chamber experiments and aerosol measurements in particular can yield valuable information about gas phase kinetics. The range obtained for the nucleation correction factor t_n is quite uncertain but tends to be near the upper limit of the bracket in Table 1, i.e. 10^3 .

The uncertainty analysis has been repeated, giving credibility to the ranges for k_1 and t_n obtained from the experiments. The results are shown in Figs 6, 7 and 8 together with the experimental points. It is shown that acceptable ranges of uncertainty are now being obtained. The remaining uncertainty on both N_{meas} and V_{meas} is now explained by the uncertainty on all four input parameters, but mainly by the uncertainty on the degree of turbulence.

The values between 10^4 and 10^7 for t_n obtained here are in marked contrast with the experimental results of Wyslouzil *et al.* (1991), from which a nucleation correction factor t_n of at most 10^{-5} can be inferred. In fact, if the latter value is used in AERO2, it is not possible to predict any particle production under the conditions of the experiments, even if the most favorable combination of k_1 , α and k_c are assumed. In the experiments of Wyslouzil *et al.* H_2SO_4 and H_2O vapours are mixed to induce nucleation and the vapours are obtained by evaporating liquid H_2SO_4 and H_2O . Hence, there is no doubt about the species that are nucleating, only about the accuracy by which the vapour concentrations can be determined at the moment of mixing. In the experiments described here H_2SO_4 is formed from the reaction between SO_2 and OH. Some evidence have been given for the fact that H_2SO_4 is the only condensable species (apart from H_2O) eventually present in the aerosol, i.e. the ion chromatographic data, the agreement between measured and calculated mass of sulphate in the aerosol, and finally the appropriate predictions by AERO2 of the number and volume concentrations in the smog experiments for times larger than 30 min. Since there is no certainty about the species involved in the initial stages of the nucleation process, the discrepancy between the values for t_n of Wyslouzil *et al.* and those from the present work could be explained in two ways:

(1) In our $\text{SO}_2\text{-NO}_x$ mixture, the reaction $\text{SO}_2 + \text{OH}$ forms intermediate sulphur or sulphur-nitrogen complexes, which catalyse new particle formation, and which are eventually hydrolysed to H_2SO_4 . The formation of H_2SO_4 is generally explained without the involvement of such complexes, however a thorough discussion of the $\text{SO}_2 + \text{OH}$ reaction cannot rule them out completely (Calvert and Stockwell, 1984).

(2) Apart from H_2SO_4 and H_2O , other condensable species such as HNO_3 and undetectable traces of others components do participate initially in a ternary or higher order nucleation process, which is faster than the binary nucleation of H_2SO_4 and H_2O . These extra species should remain present in undetectable quantities or be driven out of the particles later on.

SUMMARY

We have described a model, AERO2, which simulates the formation and growth of an $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ aerosol in a smog chamber, based on nucleation, condensation, coagulation

and wall deposition. The output of such an aerosol dynamics model is known to be sensitive to a number of input parameters, a subset of which has been selected 'a priori', namely the reaction rate between SO₂ and OH (k_1), the nucleation rate, reduced to a correction factor to the classical theory of heteromolecular homogeneous nucleation (t_n), the mass accommodation coefficient of H₂SO₄ (α), and the eddy diffusion parameter (k_e). Uncertainties on these parameters were taken from literature, and their propagation through AERO2 has been investigated. The following conclusions have been made for the conditions generally prevailing in smog chambers.

The uncertainties on the input parameters are propagated in such a way that aerosol dynamics models in general and AERO2 in particular can only predict upper bounds for the total and detectable number and volume concentrations.

The uncertainty on k_1 dominates the uncertainty on the total number and volume concentrations predicted by AERO2, except during, and immediately after, the nucleation burst where the uncertainty on t_n becomes equally important and the uncertainty on α also contributes significantly to the uncertainty on the number concentration.

Even when the uncertainty on k_1 is artificially reduced to 10%, the range of uncertainty on number and volume is a factor of 20–100, mainly caused by the uncertainty on the nucleation rate.

Because of the large uncertainties, three smog chamber experiments have been performed in an attempt to reduce the uncertainties on k_1 and t_n , based on measurements of the number and volume concentration. The findings are the following.

A range of values for k_1 is obtained between 7.8×10^{-13} and 1.0×10^{-12} cm³ s⁻¹. This range is smaller than and within the range of the literature.

The value for t_n is much larger than 1, and a range between 10⁴ and 10⁷ is proposed. There is a large uncertainty in this range, but it still suggests values that are about 10 orders of magnitude larger than the t_n needed to explain recent experiments on nucleation in H₂SO₄-H₂O mixtures. This discrepancy is discussed in the text.

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