

Parametrization of ternary nucleation rates for H₂SO₄-NH₃-H₂O vapors

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[1] A parametrization of nucleation rates for H₂O-H₂SO₄-NH₃ vapors in atmospheric conditions is developed. The parametrization is based on nucleation rates obtained from a self-consistent model of ternary nucleation, including state-of-art thermodynamics, H₂O-H₂SO₄ hydration model, and rigorous treatment of nucleation kinetics. The parametrized nucleation rates are shown to be within one order of magnitude from those given by the full model with enhanced accuracy at higher nucleation rates. Parametrizations for particle numbers and radius of the critical nucleus are given as a function of nucleation rate and temperature. The parametrizations are valid for temperatures 240–300 K, relative humidities 5–95%, sulfuric acid concentrations 10⁴–10⁹ molecules cm⁻³, ammonia mixing ratios 0.1–100 ppt, and nucleation rates 10⁻⁵–10⁶ cm⁻³ s⁻¹. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; **KEYWORDS:** water, sulfuric acid, ammonia, nucleation

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1. Introduction

[2] Experimental and theoretical progress in recent years has shown the importance of homogeneous nucleation in new particle production in the atmosphere [Weber *et al.*, 1999; Kulmala *et al.*, 2000]. In addition to water vapor, the nucleation process typically involves one or more trace compounds which may have crucial role in the formation of stable aerosol particles. In this respect the most studied example is the conucleation of water and sulfuric acid [e.g., Kulmala *et al.*, 1998; Seinfeld and Pandis, 1998]. However, in many cases the observed atmospheric particle formation rates greatly exceed those expected on the basis of binary H₂O-H₂SO₄ nucleation alone, for example, in marine [Covert *et al.*, 1992; Hoppel *et al.*, 1994] and coastal [O'Dowd *et al.*, 1999] boundary layer and in boreal forests [Mäkelä *et al.*, 1997; Kulmala *et al.*, 2001]. Although several explanations have been proposed to explain the enhanced particle production (e.g., ion-induced nucleation [Turco *et al.*, 1998]), the most obvious explanation is the participation of a third chemical component in the nucleation process [Kulmala *et al.*, 2000]. The most likely candidate is ammonia because of its abundance in the atmosphere and its ability to lower the vapor pressure H₂SO₄ above the solution, which is expected to enhance particle formation in gases containing

H₂SO₄ [Scott and Cattell, 1979; Coffmann and Hegg, 1995].

[3] In ternary nucleation rather complex thermodynamics and chemistry of H₂O-H₂SO₄-NH₃ system are needed [Napari *et al.*, 2002]. In the liquid phase, H₂SO₄ and NH₃ undergo multiple dissociation and association steps producing various salts and ions. The gas phase behavior is characterized by the formation of water-sulfuric acid hydrates in which one H₂SO₄ and one or more H₂O molecules gather into small clusters. Considering these facts, an accurate and comprehensive thermodynamic model is critical to understanding nucleation phenomena in H₂O-H₂SO₄-NH₃ vapors. Due to the complex thermodynamics and detailed nucleation kinetics [Napari *et al.*, 2002] the calculation of nucleation rate is computationally very demanding. In order to be able to use ternary nucleation scheme as a part of aerosol dynamic models or even in 3-D atmospheric models parametrizations are urgently needed.

[4] The purpose of this paper is to present an up-to-date parametrized equation for nucleation rates in H₂O-H₂SO₄-NH₃ vapors. Only those values which are obtained from a recently developed ternary nucleation model [Napari *et al.*, 2002] are used in the fitting procedure. We try to include as wide range of atmospherically relevant parameter values as possible while aiming for accuracy of one order of magnitude at significant nucleation rates.

[5] We first present the ternary nucleation model in a concise form in section 2. The parametrizations are derived in section 3. The full model and the parametrizations are compared in section 4. Finally, discussion and conclusions are presented in section 5.

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2. Ternary Nucleation Model

[6] The formation energy ΔG of a cluster in a ternary vapor can be written as [Laaksonen *et al.*, 1999]

$$\Delta G = -kT \sum_{i=1}^3 n_i \ln \left(\frac{p_i}{p_{s,i}} \right) + 4\pi\sigma r^2, \quad (1)$$

where n_i are the total number of molecules of each species in the cluster, p_i is the ambient partial pressure of free molecules of species i , $p_{s,i}$ is the equilibrium vapor pressure of species i above a flat surface of a solution with the composition of the nucleus, r is the radius of the droplet, k is Boltzmann constant, and T is temperature. The surface tension of a flat liquid-vapor interface σ is evaluated at the composition of the nucleus. In the present case indices 1, 2, and 3 refer to water, sulfuric acid, and ammonia.

[7] Minimization of equation (1) with respect of particle numbers n_i results in a pair of equations [Wilemski, 1984]

$$\ln \left(\frac{p_1}{p_{s,1}} \right) v_2 = \ln \left(\frac{p_2}{p_{s,2}} \right) v_1, \quad (2)$$

$$\ln \left(\frac{p_3}{p_{s,3}} \right) v_2 = \ln \left(\frac{p_2}{p_{s,2}} \right) v_3, \quad (3)$$

where v_i is the partial molar volume of species i . The composition of the critical nucleus is numerically solved from equations (2) and (3), and the corresponding formation energy is then found from [Laaksonen *et al.*, 1999]

$$\Delta G^* = \frac{4}{3} \pi r^{*2} \sigma, \quad (4)$$

where r^* is the radius of the critical nucleus.

[8] Once the composition is known, the nucleation rate is obtained from [Trinkaus, 1983]

$$J = \frac{|\lambda|/\pi}{\sqrt{-\det(\mathbf{D})/\pi}} \rho(\{n_i\}), \quad (5)$$

where \mathbf{D} is a matrix with elements

$$D_{ij} = \frac{1}{2kT} \frac{\partial^2 \Delta G(\{n_i\})}{\partial n_i \partial n_j} \Big|_{\{n_i^*\}} \quad (i, j = 1, 2, 3), \quad (6)$$

and λ is the negative eigenvalue of matrix \mathbf{KD} , where \mathbf{K} is the condensation matrix [Binder and Stauffer, 1976]. The elements of the condensation matrix are related to the collision rate of the vapor particles with the cluster. In our case the colliding particles are water monomers, free acid molecules, free ammonia molecules, or water-acid hydrates containing one acid molecule and up to five water molecules. The equilibrium distribution of clusters containing n_i molecules of each species $\rho(\{n_i\})$ is obtained from the self-consistent equilibrium distribution [Noppel, 2000, equation (3)]. The formation energy ΔG is obtained from equation (1) and the matrix elements in equation (6) are evaluated at the composition of the critical nucleus with particle numbers n_i^* .

[9] In the most rigorous form of equation (6) the derivatives are calculated with respect to total number of particles $n_i = n_{il} + n_{is}$, where n_{il} are the numbers of molecules in the

uniform liquid phase encompassed by the surface of tension and n_{is} are the surface excess number of molecules caused by the difference between the density profiles of the uniform Gibbsian droplet model and the actual droplet. However, because of numerical efficiency and stability, we approximate $n_i \approx n_{il}$ [Napari *et al.*, 2002]; that is, we assume that derivatives do not depend on the surface excess number of particles. The resulting errors in nucleation rates are less than half an order of magnitude.

[10] The calculation of the partial pressures of H_2O and NH_3 is based on the thermodynamic model of Clegg *et al.* [1998] (available as <http://www.hpc1.uea.ac.uk/~e770/aim.html>). The partial pressure of H_2SO_4 is estimated as described by Noppel *et al.* [2002]. Details of the hydration model are given by Napari *et al.* [2002] and Noppel *et al.* [2002]. Surface tension and density of the solution are approximated using the method of Van Dingenen and Raes [1993]; however, instead of direct application of this method to H_2O - H_2SO_4 - NH_3 system, surface tension and density are also fitted to binary limits of $(\text{NH}_4)_2\text{SO}_4$ - H_2O and NH_4HSO_4 - H_2O [Korhonen *et al.*, 1999].

3. Parametrization of Nucleation Rate Values

[11] In this section we present a parametrization of ternary nucleation rates $J(T, RH, c, \xi)$, where T is temperature, RH is relative humidity, c is H_2SO_4 concentration, and ξ is NH_3 mixing ratio. In addition, we give the number of different types of molecules in the critical nuclei and the radius of the nuclei as a function of nucleation rate and temperature. The parametrizations are based on data generated using the full nucleation model outlined in the previous section.

[12] In order to construct the parametrization for nucleation rate we first searched for functional dependencies by keeping three variables constant at a time. We soon found that a polynomial fit reproduced the nucleation rates at a constant temperature quite accurately if polynomials of RH , $\ln RH$, $\ln c$, $1/\ln c$, and $\ln \xi$ were used in the fitting. However, the temperature dependence was harder to fit according to this scheme, because at high temperatures nucleation rate is a very strong function of temperature whereas at low temperatures the temperature dependence is virtually nonexistent [Napari *et al.*, 2002]. Notwithstanding, we were able to account for the temperature dependence of the coefficients in the aforementioned polynomial expansion by fitting each of the coefficients to a third-order polynomial of temperature.

[13] The resulting fit has the form

$$\begin{aligned} \ln J_{\text{fit}} = & -84.7551 + \frac{f_1(T)}{\ln c} + f_2(T) \ln c + f_3(T) \ln^2 c + f_4(T) \ln \xi \\ & + f_5(T) \ln^2 \xi + f_6(T) RH + f_7(T) \ln RH + f_8(T) \frac{\ln \xi}{\ln c} \\ & + f_9(T) \ln \xi \ln c + f_{10}(T) RH \ln c + f_{11}(T) \frac{RH}{\ln c} \\ & + f_{12}(T) RH \ln \xi + f_{13}(T) \frac{\ln RH}{\ln c} + f_{14}(T) \ln RH \ln \xi \\ & + f_{15}(T) \frac{\ln^2 \xi}{\ln c} + f_{16}(T) \ln c \ln^2 \xi + f_{17}(T) \ln^2 c \ln \xi \\ & + f_{18}(T) RH \ln^2 \xi + f_{19}(T) \frac{RH \ln \xi}{\ln c} + f_{20}(T) \ln^2 c \ln^2 \xi, \quad (7) \end{aligned}$$

Table 1. Coefficients of Polynomials $f_i(T)$

i	a_{i0}	a_{i1}	a_{i2}	a_{i3}
1	-0.355297	-33.8449	0.34536	-0.000824007
2	3.13735	-0.772861	0.00561204	-9.74576E-6
3	19.0359	-0.170957	0.000479808	-4.14699E-7
4	1.07605	1.48932	-0.00796052	7.61229E-6
5	6.0916	-1.25378	0.00939836	-0.0000174927
6	0.31176	1.64009	-0.00343852	-0.0000109753
7	-0.0200738	-0.752115	0.00525813	-8.98038E-6
8	0.165536	3.26623	-0.0489703	0.000146967
9	6.52645	-0.258002	0.00143456	-2.02036E-6
10	3.68024	-0.204098	0.00106259	-1.2656E-6
11	-0.066514	-7.82382	0.0122938	0.0000618554
12	0.65874	0.190542	-0.00165718	3.41744E-6
13	0.0599321	5.96475	-0.0362432	0.0000493337
14	-0.732731	-0.0184179	0.000147186	-2.37711E-7
15	0.728429	3.64736	-0.027422	0.0000493478
16	41.3016	-0.35752	0.000904383	-5.73788E-7
17	-0.160336	0.00889881	-0.0000539514	8.39522E-8
18	8.57868	-0.112358	0.000472626	-6.48365E-7
19	0.0530167	-1.98815	0.0157827	-0.0000293564
20	-2.32736	0.0234646	-0.000076519	8.0459E-8

Read E-x as 10^{-x} .

where each of the functions $f_i(T)$ is a third-order polynomial

$$f_i(T) = a_{i0} + a_{i1}T + a_{i2}T^2 + a_{i3}T^3. \quad (8)$$

The coefficients a_{ij} are listed in Table 1. Temperature is given in kelvins, H_2SO_4 concentration in cm^{-3} , NH_3 mixing ratio in ppt, and relative humidity as a fraction (e.g., 0.5 corresponding to 50%). Nucleation rate is then obtained in $\text{cm}^{-3} \text{s}^{-1}$.

[14] The limits of validity of the parametrization are $T = 240\text{--}300$ K, $RH = 0.05\text{--}0.95$, $c = 10^4\text{--}10^9 \text{cm}^{-3}$, $\xi = 0.1\text{--}100$ ppt, and $J = 10^{-5}\text{--}10^6 \text{cm}^{-3} \text{s}^{-1}$. The upper limit of nucleation rate is particularly stringent due to the polynomial fit; the parametrized curve as a function of temperature may show an erroneous minimum at low temperatures if nucleation rate exceeds the limit of validity. Also, because of the logarithmic dependencies on RH and c , the parametrization cannot be used to obtain binary $\text{H}_2\text{O}\text{--}\text{H}_2\text{SO}_4$ or $\text{H}_2\text{O}\text{--}\text{NH}_3$ limit.

[15] Approximations for the number of particles of each molecular species in the critical nucleus n_i^* and the radius the cluster r^* can easily be obtained as functions of nucleation rate and temperature:

$$n_{\text{H}_2\text{SO}_4}^* = 38.1645 + 0.774106 \ln J + 0.00298879 \ln^2 J - 0.357605T - 0.00366358T \ln J + 0.0008553T^2, \quad (9)$$

$$n_{\text{NH}_3}^* = 26.8982 + 0.682905 \ln J + 0.00357521 \ln^2 J - 0.265748T - 0.00341895T \ln J + 0.000673454T^2, \quad (10)$$

$$n_{\text{tot}}^* = 79.3484 + 1.7384 \ln J + 0.00711403 \ln^2 J - 0.744993T - 0.00820608T \ln J + 0.0017855T^2, \quad (11)$$

$$r^* = 0.141027 - 0.00122625 \ln J - 7.82211 \times 10^{-6} \ln^2 J - 0.00156727T - 0.00003076T \ln J + 0.0000108375T^2. \quad (12)$$

where $n_{\text{H}_2\text{SO}_4}^*$, $n_{\text{NH}_3}^*$, and n_{tot}^* are the numbers (including the surface excess numbers) of H_2SO_4 , NH_3 , and the total number of particles, respectively. Nucleation rate is given in

$\text{cm}^{-3} \text{s}^{-1}$ and temperature in kelvins. The critical radius is obtained in nanometers. As above, validity of the parametrizations is limited to nucleation rates $J = 10^{-5}\text{--}10^6 \text{cm}^{-3} \text{s}^{-1}$ and temperatures $T = 240\text{--}300$ K. The number water of molecules cannot be fitted according to this simple scheme; however, the water content of the critical clusters in the nucleation rate range considered here is usually less than 0.5 molecules at low temperatures, and can thus be set to zero. At temperatures higher than about 280 K a reasonable estimate of the water content is obtained by subtracting the fitted $n_{\text{H}_2\text{SO}_4}^*$ and $n_{\text{NH}_3}^*$ from n_{tot}^* .

4. Results

[16] The ratio of the fitted nucleation rate (7) and the nucleation rate from the full ternary nucleation model are shown in Figure 1. The parameter values vary over their full range of validity. For nucleation rates higher than $10^{-3} \text{cm}^{-3} \text{s}^{-1}$, 75% of the ratios J_{fit}/J are in the range 0.53–1.47 and 95% in the range 0.26–1.74. For $J = 10^{-6}\text{--}10^{-4} \text{cm}^{-3} \text{s}^{-1}$ the deviation is somewhat larger, but at such low nucleation rates the reduced accuracy is of lesser consequence. For the whole range of nucleation rates and parameter values we can safely assume that the parametrization is correct to one order of magnitude almost everywhere.

[17] Comparisons of the parametrization for the nucleation rate and the full model calculations at temperatures 258.15 K and 298.15 K are shown in Figures 2–4. In each figure the results from equation (7) are indicated as dotted lines. Figure 2 illustrates the dependence of nucleation rate on total H_2SO_4 concentration (free H_2SO_4 molecules and H_2SO_4 in hydrates) for a pair of NH_3 mixing ratios for both the temperatures. The overall goodness of the fit can be considered as excellent. A similar plot is shown in Figure 3 depicting the dependence of nucleation rate on NH_3 mixing ratio. The largest deviation here is just over one order of

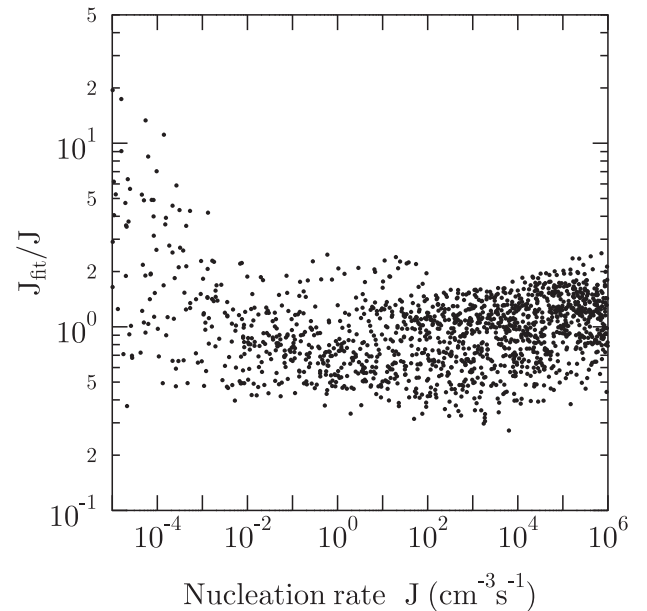


Figure 1. Ratio of the fitted nucleation rate J_{fit} and the theoretical nucleation rate J . The parameter ranges are $T = 240\text{--}300$ K, $RH = 0.05\text{--}0.95$, $c = 10^4\text{--}10^9$ molecules cm^{-3} , $\xi = 0.1\text{--}100$ ppt.

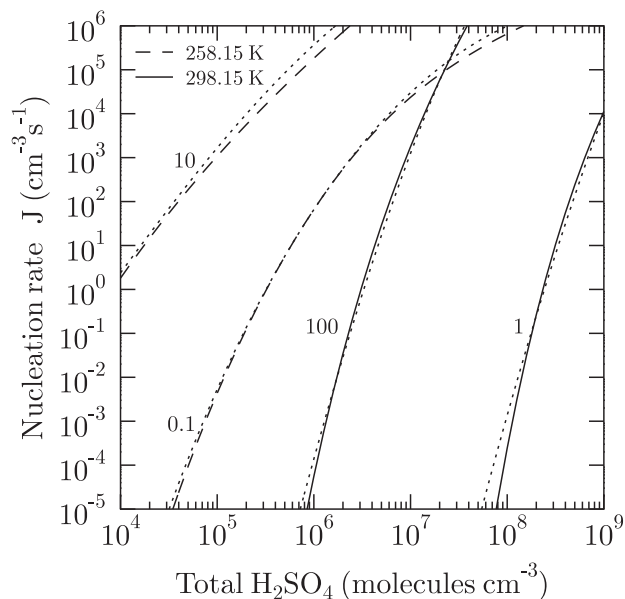


Figure 2. Nucleation rate as a function of total H_2SO_4 concentration at $T = 258.15 \text{ K}$ and $T = 298.15 \text{ K}$. Ammonia mixing ratio (in ppt) is indicated for each curve. Nucleation rates obtained from the parametrization are depicted as a dotted line. Relative humidity is 50%.

magnitude. Nucleation rate as a function of relative humidity is shown in Figure 4. The poorest fit is found for the curve with $T = 298.15 \text{ K}$ and $\xi = 10 \text{ ppt}$. Fortunately, the largest discrepancy (about one order of magnitude) occurs at low nucleation rates where larger errors are acceptable. At higher nucleation rates an almost perfect fit is obtained.

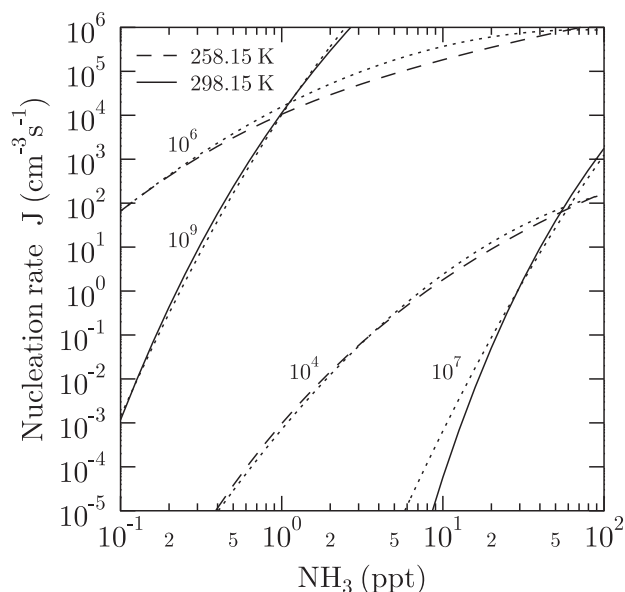


Figure 3. Nucleation rate as a function of ammonia mixing ratio at $T = 258.15 \text{ K}$ and $T = 298.15 \text{ K}$. Total sulfuric acid concentration (in molecules cm^{-3}) is indicated for each curve. Parametrizations are shown as dotted lines. Relative humidity is 50%.

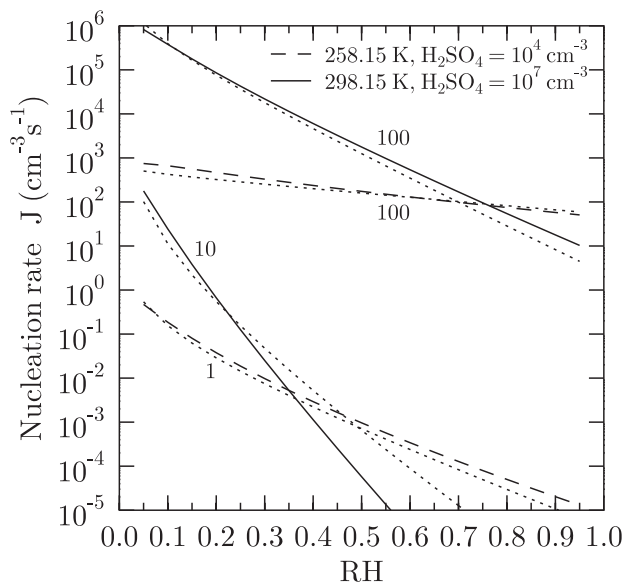


Figure 4. Dependence of nucleation rate on relative humidity at $T = 258.15 \text{ K}$ and $T = 298.15 \text{ K}$. Ammonia mixing ratio (in ppt) is indicated in the figure. Parametrizations are shown as dotted lines.

[18] A common property of Figures 2–4 is that the parametrization is worst at the higher temperature as nucleation rate approaches the lower limit. This reflects the fact that nucleation rate is a strong function of temperature at low nucleation rates, as shown in Figure 5. Also problematic is the inclusion of near-constancy of nucleation rate in the parametrization at low temperatures; nevertheless, the difference between the model and the parametrization is less than about one order of magnitude for all temperatures.

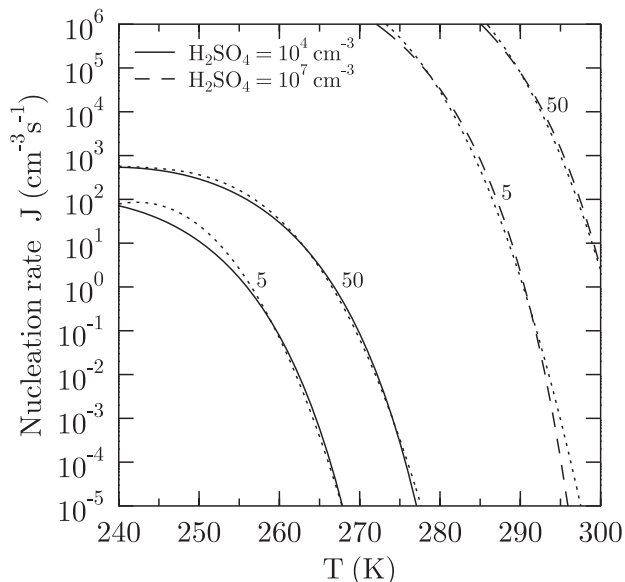


Figure 5. Temperature dependence of nucleation rate. Ammonia mixing ratio (in ppt) is indicated for each curve. Relative humidity is 50%. Parametrizations are shown as dotted lines.

[19] Figure 6 shows the number of H_2SO_4 molecules (Figure 6a), number of NH_3 molecules (Figure 6b), total number of molecules (Figure 6c), and the radius of the critical cluster (Figure 6d) as a function of nucleation rate at $T = 280$ K. The parametrizations from equations (9)–(12) (lines) are compared to model data (dots). The number of H_2SO_4 and NH_3 molecules are almost the same for all the cases considered here. At $T = 280$ K the total number of molecules in the critical cluster is practically the same as the sum of the H_2SO_4 and NH_3 molecules, because the number of water molecules is very small (usually less than 1, which can be rounded off to zero). The parametrizations give the particle content with a typical accuracy of one molecule. The difference between the radii from the full nucleation model and the parametrization is about 0.05 nm. The accuracy of the fits (9)–(12) have little dependence on temperature or cluster size.

5. Discussion and Conclusions

[20] We have constructed a parametrization of H_2O - H_2SO_4 - NH_3 nucleation rates. The parametrization covers gas abundances commonly observed in the troposphere, including upper troposphere. However, the temperature range is somewhat limited at the lower end because the nucleation model is not valid at low temperatures (typically below 240 K). The very highest temperatures ($T > 300$ K) are omitted because it was impossible to include a wider temperature range in the same fit. Also, we have set the upper limit of ammonia mixing ratio to 100 ppt. This is partly because ammonia mixing ratios greater than 100 ppt do not have much effect on nucleation rate unless H_2SO_4 concentration is very low, partly because a wider range of mixing ratios would make the parametrizations worse. If ammonia mixing ratio exceeds 100 ppt, we recommend using values obtained with 100 ppt.

[21] The parametrization reproduces the nucleation rates obtained from the full model usually within the range of one order of magnitude in general. The fit is worst at high temperatures and low nucleation rates. We do not consider this as a serious problem, because at significant nucleation rates ($J > 0.01$ – $0.1 \text{ cm}^{-3} \text{ s}^{-1}$) the fit is more accurate and, thus, adequate for atmospherically related purposes.

[22] No matter how good is the parametrization, there still is a question of the validity of nucleation model itself, and ultimately the model should be compared to experiments. Unfortunately, there is no experimental data available for such a comparison. However, we know that classical nucleation model fails close to the binary H_2O - H_2SO_4 limit [Napari *et al.*, 2002]. Therefore, we have excluded the data points with less than 0.1 ppt of ammonia from our parametrizations.

[23] The presented parametrization is the first relevant parametrization for ternary nucleation rates and it can be

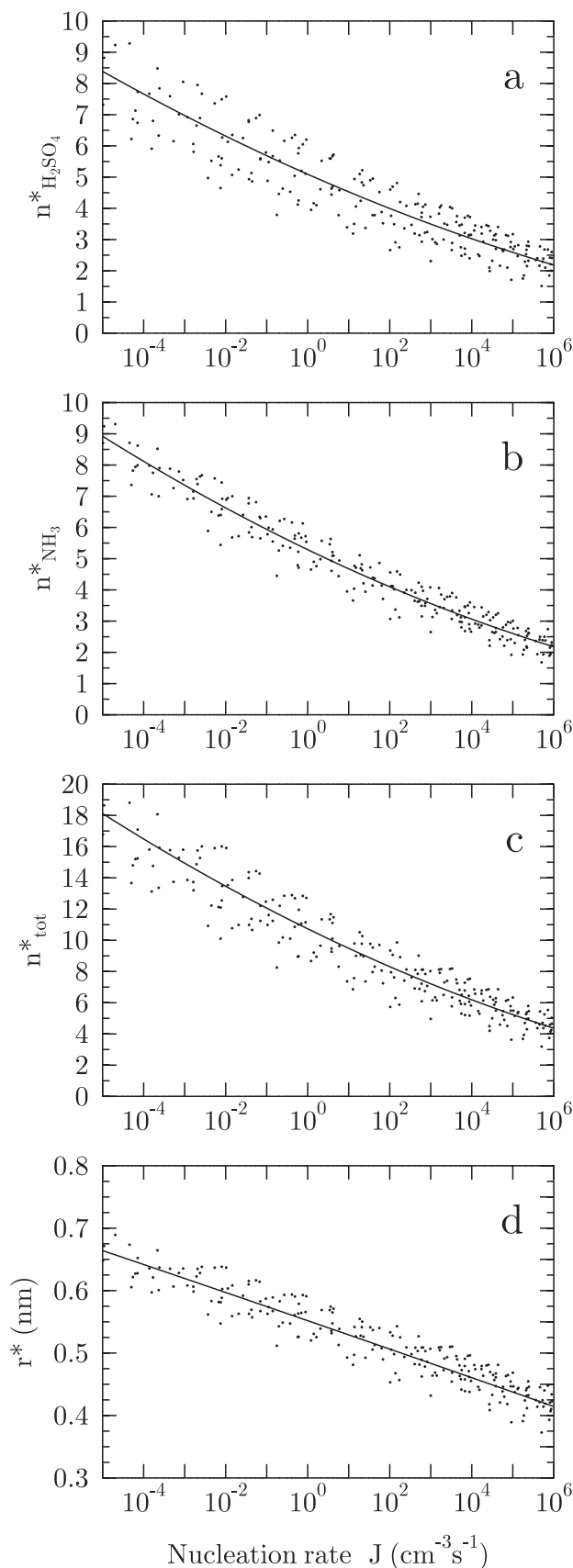


Figure 6. (opposite) Number of H_2SO_4 molecules (a), number of NH_3 molecules (b), total number of molecules (c) in the critical cluster, and the radius of the critical nucleus (d) as a function of nucleation rate at $T = 280$ K. Dots describe data from the full model while the lines are parametrizations. The gas concentrations in each plot are within the limits given in the text.

used as a subroutine for different types of aerosol dynamic models. Compared with the full model it saves computing time by a factor of 10^5 .

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