

An improved model for ternary nucleation of sulfuric acid–ammonia–water

I. Napari^{a)}

Department of Physical Sciences, P.O. Box 64, 00014 University of Helsinki, Finland

M. Noppel

Department of Physical Sciences, P.O. Box 64, 00014 University of Helsinki, Finland, and Institute of Environmental Physics, University of Tartu, 18 Ülikooli Str. 50090 Tartu, Estonia

H. Vehkamäki and M. Kulmala

Department of Physical Sciences, P.O. Box 64, 00014 University of Helsinki, Finland

(Received 3 October 2001; accepted 20 December 2001)

A revised homogeneous ternary nucleation model in H_2O – H_2SO_4 – NH_3 vapors is presented. The model is based on a self-consistent version of classical nucleation theory with a rigorous treatment of nucleation kinetics. The calculation of equilibrium vapor pressures is completely revised and the effect of H_2O – H_2SO_4 hydration is considered in detail. Compared to earlier models, the new model is able to predict nucleation rates over a wider range of temperatures and trace gas concentrations. A considerable dependence on relative humidity is found. The critical clusters corresponding to significant nucleation rates typically contain less than ten molecules and consist almost exclusively of H_2SO_4 and NH_3 . © 2002 American Institute of Physics. [DOI: 10.1063/1.1450557]

I. INTRODUCTION

Experimental and theoretical progress in recent years has showed the importance of homogeneous nucleation in new particle production in the atmosphere.^{1,2} 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 droplets. In this respect the most studied example is the conucleation of water and sulfuric acid which has been assumed a major mechanism of particle production in many atmospheric conditions.^{3,4}

However, in many cases the observed rates of particle formation greatly exceed those expected on the basis of binary H_2O – H_2SO_4 nucleation alone, for example, in marine^{5,6} and coastal⁷ boundary layers and in boreal forests.⁸ Although several processes have been proposed to explain this particle production, along with meteorological-related nucleation enhancement processes such as turbulent fluctuations, waves, and mixing,^{9,10} the most obvious explanation is the participation of a third component in the nucleation process. The most likely candidate species is ammonia (NH_3) because of its abundance in the atmosphere and its ability to lower the vapor pressure H_2SO_4 above the solution, which is expected to enhance particle formation in gases containing H_2SO_4 .^{11,12}

The generalization of classical nucleation theory from binary to ternary nucleation is complicated by the rather involved thermodynamics and chemistry of H_2O – H_2SO_4 – NH_3 system. In the liquid phase, H_2SO_4 and NH_3 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 H_2SO_4 and one or more H_2O molecules gather into small clusters. Hydrates have negative formation energy and it is,

therefore, energetically more difficult to form a critical cluster out of hydrates than out of free molecules. Considering these facts, an accurate and comprehensive thermodynamical model is critical to understanding nucleation phenomena in H_2O – H_2SO_4 – NH_3 vapors.

Our first quantification of ternary nucleation in H_2O – H_2SO_4 – NH_3 system¹³ showed that the presence of ammonia does enhance homogeneous nucleation rates by several orders of magnitude, which is in line with preliminary experimental findings.¹⁴ However, the model was only applicable at temperatures close to 298 K. In a subsequent version we increased the temperature range and improved the thermodynamical part¹⁵ but the model was still afflicted with several problems of mostly numerical origin. Also, we did not consider the formation of hydrates explicitly.

In this study, we present a completely revised model of ternary H_2O – H_2SO_4 – NH_3 nucleation. The thermodynamical part has been replaced with a state-of-the-art model by Clegg *et al.*¹⁶ which gives equilibrium vapor pressures closer to experimental values. Omitted from previous versions, hydrate correction is now incorporated in the model using a novel method by Noppel *et al.*¹⁷ The basic theoretical apparatus is based on a self-consistent version of classical nucleation theory with a cluster distribution obeying the law of mass action. Furthermore, nucleation kinetics are treated in a rigorous manner.

This paper is organized as follows. In Sec. II A, we introduce the fundamental equations of classical nucleation theory needed to determine the composition of a critical nucleus in a ternary system. Nucleation kinetics required for the evaluation of nucleation rate are elaborated in Sec. II B. A numerical comparison of three different methods for the calculation of the kinetic factor are presented. Section III is devoted to results of our calculations in atmospheric condi-

^{a)}Author to whom correspondence should be addressed.

tions. A comparison with a previous study is made. Discussion and conclusions are presented in Sec. IV.

II. THEORY

A. Composition of the critical cluster

Consider a cluster (not necessarily critical) containing n_1 molecules of water, n_2 molecules of sulfuric acid, and n_3 molecules of ammonia. The formation energy of the cluster is assumed to be given by¹⁸

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

where 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 solution surface, r is the radius of the droplet, and σ is the surface tension of a flat liquid–vapor interface at the composition of the nucleus. The total numbers of molecules in the nucleus n_i are

$$n_i = n_{il} + n_{is}, \quad (2)$$

where n_{il} are the numbers of molecules in the uniform liquid phase encompassed by the surface of tension and n_{is} is the surface excess number of molecules arising from the difference between the density profiles of the uniform Gibbsian droplet model and the actual droplet.

Setting $(\partial\Delta G/\partial n_i)_{n_j} = 0$ yields two coupled equations

$$\ln \left(\frac{p_1}{p_{s,1}} \right) v_2 = \ln \left(\frac{p_2}{p_{s,2}} \right) v_1, \quad (3)$$

$$\ln \left(\frac{p_3}{p_{s,3}} \right) v_2 = \ln \left(\frac{p_2}{p_{s,2}} \right) v_3, \quad (4)$$

where v_i is the partial molar volume of species i . The composition of the critical cluster is found by solving Eqs. (3) and (4) numerically. Within the limits of capillarity approximation the radius of the critical cluster is then obtained from Kelvin equation,

$$r^* = \frac{2\sigma v_i}{kT \ln \left(\frac{p_i}{p_{s,i}} \right)} \quad (5)$$

and the formation energy is given by

$$\Delta G^* = \frac{4}{3}\pi r^{*2}\sigma. \quad (6)$$

The partial pressures of H₂O and NH₃ are obtained from the thermodynamical model of Clegg *et al.*¹⁶ (<http://www.hpc1.uea.ac.uk/~e770/aim.html>). The partial pressure of H₂SO₄ is estimated as in Noppel *et al.*¹⁷ Instead of direct application of acid activity by Clegg *et al.*,¹⁶ the ratio of the activity to the activity of pure sulfuric acid (both estimated by the model of Clegg *et al.*¹⁶) is used as acid activity with respect to the reference state of pure liquid acid. In practice pure acid was represented by a solution with H₂SO₄ molality of 10⁷ mol/kg. The partial pressure of free sulfuric acid is then calculated by multiplication of the obtained acid activity with the pressure value of pure acid. The latter is taken from Noppel *et al.*¹⁷ and it is based on the fitting to the values of

Ayers *et al.*¹⁹ corrected by Kulmala and Laaksonen,²⁰ and the total acid pressure values measured by Marti *et al.*²¹ The density and surface tension of the ternary solution is calculated applying the method of Van Dingenen and Raes²² modified to produce correct values at the limits of (NH₄)₂SO₄–H₂O and NH₄HSO₄–H₂O.^{13,23}

The present thermodynamical model differs in one important respect from the one used in our previous studies on ternary nucleation:^{13,15} complete transformation of NH₃ into NH₄⁺ is assumed in the liquid phase. We do not believe this to be a significant restriction in nucleation calculations because (on the basis of this and our earlier studies) the solution corresponding the composition of critical nuclei is always acidic and, as such, contains enough H⁺ ions for the transformation.

B. Nucleation rate

In its most general form nucleation rate is given by²⁴

$$J = \frac{|\lambda|/\pi}{\sqrt{-\det(\mathbf{D})/\pi}} \rho(\{n_i\}), \quad (7)$$

where $\rho(\{n_i\})$ is the equilibrium distribution of clusters containing n_i molecules of each species, \mathbf{D} is a matrix with elements

$$D_{ij} = \frac{1}{2kT} \left. \frac{\partial^2 \Delta G(\{n_i\})}{\partial n_i \partial n_j} \right|_{\{n_i^*\}} \quad (i, j = 1, 2, 3), \quad (8)$$

and λ is the negative eigenvalue of matrix \mathbf{KD} , where \mathbf{K} is the condensation matrix²⁵

$$K_{mn} = \sum_{\{n_i^*\}}^{\xi} n'_m n'_n k(\{n_i^*\}; \{n_i^*\}) \rho(\{n_i^*\}), \quad (9)$$

where $k(\{n_i^*\}; \{n_i^*\})$ is the rate of collisions between critical clusters of size $(\{n_i^*\})$ and clusters of size $(\{n_i^*\})$, n'_m and n'_n are the numbers of molecules of species m and n ($m, n = 1, 2, 3; 1 = \text{H}_2\text{O}, 2 = \text{H}_2\text{SO}_4, 3 = \text{NH}_3$) in a cluster of size $(\{n_i^*\})$, respectively. Summation in Eq. (9) goes over all clusters up to ξ , which is an upper bound above which cluster–cluster collisions are neglected. In this paper, the colliding clusters are assumed to be water monomers ($i' = 1, j' = 0, k' = 0$), free acid molecules ($i' = 0, j' = 1, k' = 0$), free ammonia molecules ($i' = 0, j' = 0, k' = 1$), or hydrates containing one acid molecule and at most five water molecules ($i' = 1, \dots, 5, j' = 1, k' = 0$).

From kinetic gas theory the collision probability is obtained as

$$k(\{n_i^*\}; \{n_i^*\}) = \sqrt{8\pi kT \left(\frac{1}{m^*} + \frac{1}{m'} \right)} (r^* + r'), \quad (10)$$

where r^* and r' are the radii of the critical cluster and the colliding cluster, respectively, and m^* and m' are the corresponding masses.

The equilibrium distribution is given by²⁶

$$\rho(\{n_i\}) = \rho_2 \left(\frac{\rho_1}{\rho_0} \right)^2 K_1 K_2 \exp \left(- \frac{\Delta G(\{n_i\}) - \Delta G(2,1,0)}{kT} \right), \quad (11)$$

where ρ_1 and ρ_2 are the number densities of free H₂O and H₂SO₄ molecules, respectively, ρ_0 is the number density corresponding to the reference pressure 1 atm, and K_1K_2 is the equilibrium constant for acid dihydrate formation which is estimated semiexperimentally.¹⁷ We note that this distribution is different from the conventional form of Reiss²⁷ which does not obey the mass action law²⁸ and, as a consequence, overestimates the dependence of nucleation rate on relative humidity.¹⁷

The numerical calculation of the derivatives in Eq. (8) involves evaluating ΔG when small changes are introduced to the total number of molecules n_i . Unfortunately, the thermodynamical quantities in Eq. (1) are functions of the bulk mole fractions which can be calculated only after the surface excess number of particles n_{is} are subtracted from the total number of particles. Thus, the most rigorous evaluation of the matrix elements D_{ij} requires a careful assessment of n_{is} in every step of the calculation.

If surface tension is assumed independent of curvature, the surface excess number of molecules are bound by the condition¹⁸

$$\sum_i n_{is}v_i = 0 \tag{12}$$

and volume of the cluster is given by

$$V = \frac{4\pi}{3} r^3 = \sum_i n_i v_i = \sum_i n_{il} v_i. \tag{13}$$

The numbers of molecules in the bulk phase are then expressed as

$$n_{il} = \frac{Vx_i}{\sum_i v_i x_i}, \tag{14}$$

where x_i are the bulk mole fractions. Equation (12) together with the Gibbs adsorption isotherm

$$\sum_i n_{is} d\mu_{il} + 4\pi r^2 d\sigma = 0, \tag{15}$$

yields

$$n_{is} = \frac{4\pi r^2 \sum_{j,k} \epsilon_{ijk} \left(\frac{\partial \mu_{jl}}{\partial x_2} \frac{\partial \sigma}{\partial x_3} - \frac{\partial \mu_{jl}}{\partial x_3} \frac{\partial \sigma}{\partial x_2} \right) v_k}{\sum_{j,k,m} \epsilon_{jkm} \frac{\partial \mu_{kl}}{\partial x_2} \frac{\partial \mu_{ml}}{\partial x_3} v_j}, \tag{16}$$

where the symbol $\epsilon_{ijk}=0$ if any of the indices are equal; otherwise $\epsilon_{ijk}=1$ for even permutations and $\epsilon_{ijk}=-1$ for odd permutations of indices 1, 2, 3. The chemical potential of species i in the uniform liquid phase with pressure p_l is given by

$$\mu_{il}(p_l, x_2, x_3) = \mu_{iv}(p_v, x_2, x_3) - kT \ln \left(\frac{p_i}{p_{s,i}} \right) + \frac{2v_i \sigma}{r}, \tag{17}$$

where $\mu_{iv}(p_v, x_2, x_3)$ is the chemical potential of the vapor. The core composition of any cluster with total number of molecules n_i is then obtained from Eqs. (13), (14), and (16).

Alternatively, matrix elements D_{ij} can be approximated as

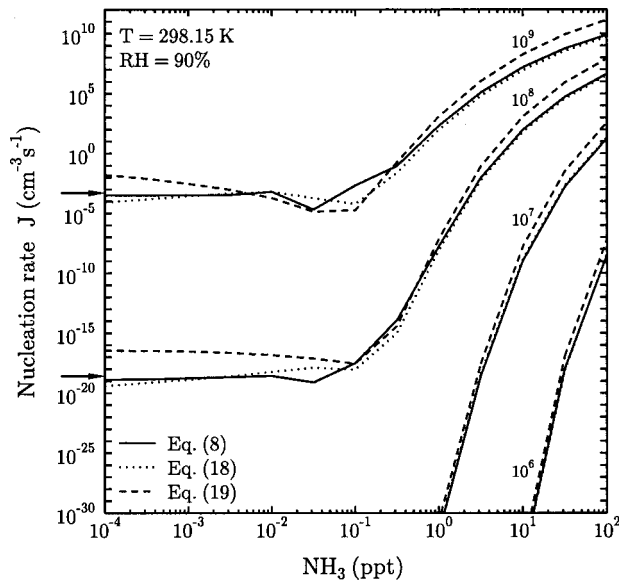


FIG. 1. Dependence of nucleation rate on ammonia mixing ratio at $T = 298.15$ K and $RH = 90\%$ for total sulfuric acid concentrations between 10^6 and 10^9 cm⁻³. Three methods of calculating the kinetic prefactor are compared (see text for details). The limit of binary water-sulfuric acid nucleation is indicated with arrows for total H₂SO₄ concentrations of 10^8 and 10^9 cm⁻³.

$$D_{ij} = \frac{1}{2kT} \left. \frac{\partial^2 \Delta G(\{n_{il}\})}{\partial n_{il} \partial n_{jl}} \right|_{\{n_{il}^*\}} \quad (i, j = 1, 2, 3), \tag{18}$$

i.e., the differentiation is performed with respect to bulk number of particles. The motivation behind this approximation lies in the efficiency of the computer code; the calculation takes many times longer if the kinetic part in Eq. (7) is calculated exactly.

A further approximation based on the concept of virtual monomer is presented in Ref. 23. In this approach, the nucleation rate is written as

$$J = R_{av} \left(\frac{\sigma v^2}{4\pi^2 k T r^4} \right)^{(1-n/2)} \rho(\{n_{ij}\}), \tag{19}$$

where R_{av} is the average growth rate, v is the volume of the virtual monomer and n is the number of molecular components. This approximation has been used in our previous studies on the ternary nucleation of H₂O-H₂SO₄-NH₃ system.^{13,15}

A comparison of nucleation rates obtained from Eqs. (8), (18), and (19) is presented in Fig. 1. It can be seen that the approximation of Eq. (18) gives an estimate of nucleation rate which is accurate enough for all practical purposes, whereas the approximation of Eq. (19) succeeds less well; this is especially true for the binary H₂O-H₂SO₄ limit. [The binary calculations were performed with a specially designed binary nucleation program using the rigorous form of Eq. (8).] Some of the wiggleness in the nucleation rate curves is probably caused by numerical inaccuracies in the calculation of derivatives in Eqs. (8) and (18) but the minima observed at ammonia mixing ratios of 0.01-0.1 ppt seem to be related to the inapplicability of classical nucleation theory at certain compositions and, thus, are not caused by the kinetic prefac-

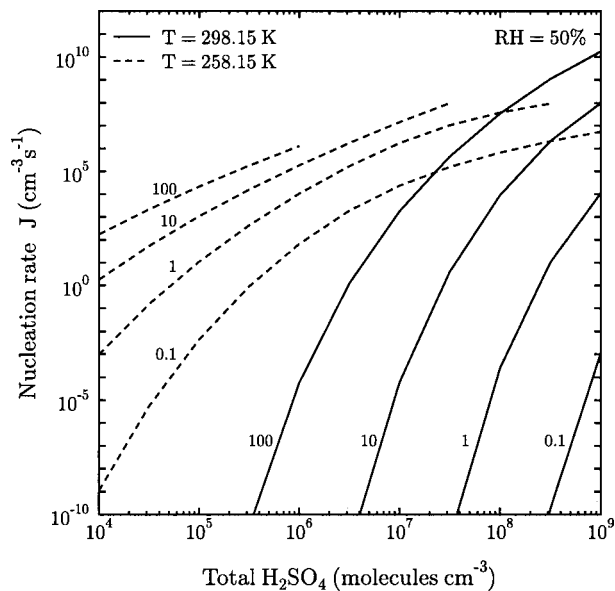


FIG. 2. Nucleation rate as a function of total sulfuric acid concentration. Ammonia mixing ratio (in ppt) is indicated for each curve.

tor. The mole fraction of ammonia in the critical nuclei changes rapidly from <0.1 to ≈ 0.4 as ammonia mixing ratio increases from about 0.01 ppt to 0.1 ppt. This kind of compositional change is a typical situation where classical nucleation theory breaks down.²⁹ Our conclusion is further strengthened by a sudden increase in $|n_{is}/n_i|$ ratios. Thus, the results for ammonia mixing ratios less than 0.1 ppt are unreliable and, therefore, are excluded from the ensuing calculations in those cases where a significant compositional change is seen.

The approximation of Eq. (18) is unsuitable for highly surface active systems, such as aqueous mixtures of organic compounds (e.g., ethanol), because the total numbers of particles n_i are very different from the bulk liquid values n_{il} .

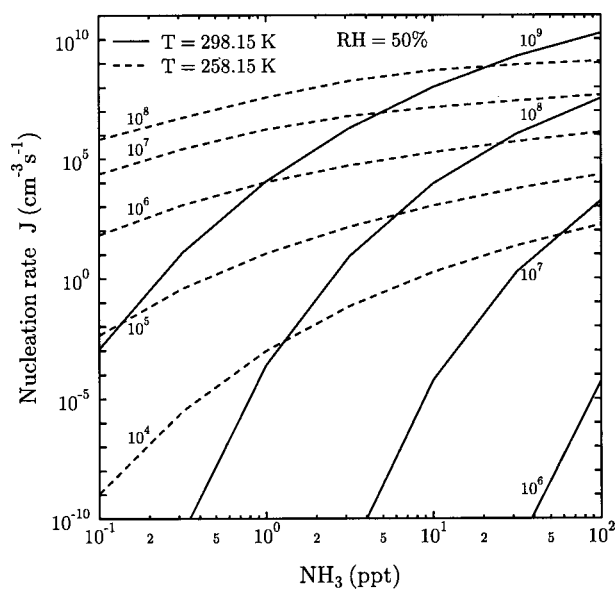


FIG. 3. Nucleation rate as a function of ammonia mixing ratio. Total sulfuric acid concentration (in cm^{-3}) is indicated for each curve.

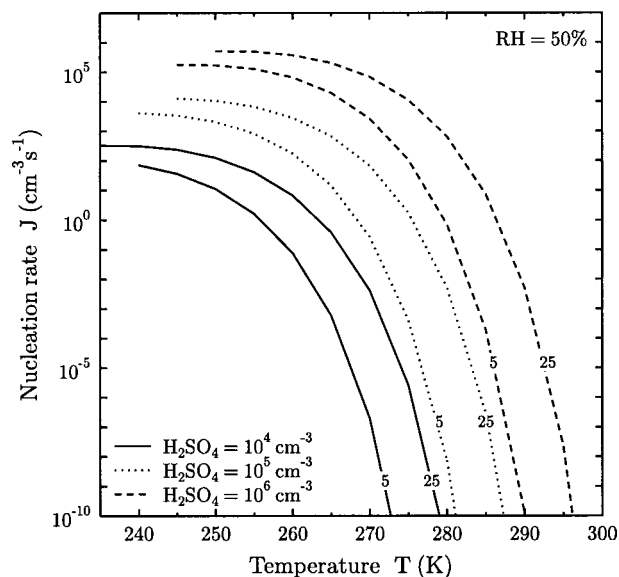


FIG. 4. Nucleation rate as a function of temperature for three total sulfuric acid concentrations at $RH=50\%$. Results for ammonia mixing ratios of 5 ppt and 25 ppt are depicted in each case.

However, the exact formula (8) can be even less applicable in these cases. Owing to the capillarity approximation used in Eq. (16) the absolute values of the excess numbers of particles n_{is} may be large enough to yield negative total number of particles for some component species, thus rendering Eq. (8) useless.

III. RESULTS

The results of our ternary nucleation calculations for different combinations of H_2SO_4 and NH_3 concentrations, relative humidity (RH) and temperature at atmospheric pressure

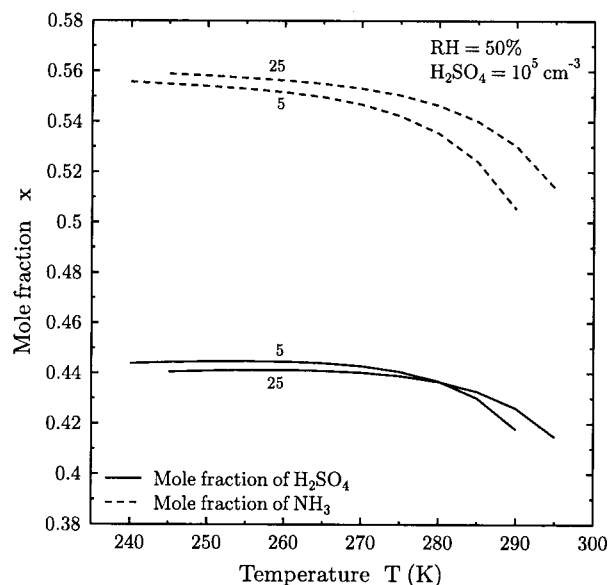


FIG. 5. Bulk mole fraction of sulfuric acid and ammonia in the critical nuclei as a function of temperature at $RH=50\%$ and total sulfuric acid concentration of 10^5 cm^{-3} . The curves correspond to ammonia mixing ratios of 5 ppt and 25 ppt.

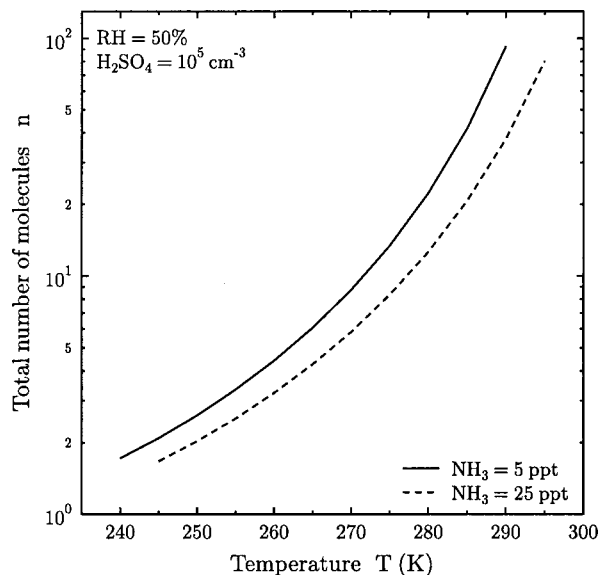


FIG. 6. Total number of molecules in the critical nuclei. The ambient conditions are the same as in Fig. 5.

are presented in Figs. 2–9. We have limited the range of parameters to those values which are relevant in atmospheric conditions: we only consider temperatures lower than 298 K, H_2SO_4 concentrations between 10^4 and 10^9 cm^{-3} , NH_3 mixing ratios under 100 ppt (corresponding to $<2.5 \times 10^9 \text{ molecules cm}^{-3}$ at atmospheric pressure), and relative humidities from 5% to 95%. The calculations were performed using Eq. (18). Values corresponding to critical clusters with the molecular content close to a single molecule are excluded from the plots (typically found in unrealistically high vapor concentrations of H_2SO_4 and NH_3). Also, clusters with the mole fraction of water less than 0.0001 are omitted,

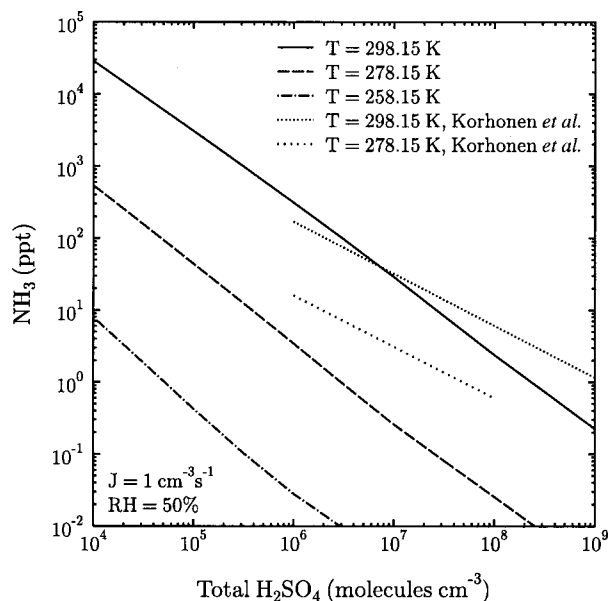


FIG. 7. Total sulfuric acid and ammonia abundances required for a constant nucleation rate of $J = 1 \text{ cm}^{-3} \text{ s}^{-1}$ at $\text{RH} = 50\%$. Also shown are corresponding calculations from Ref. 13 (see text for details).

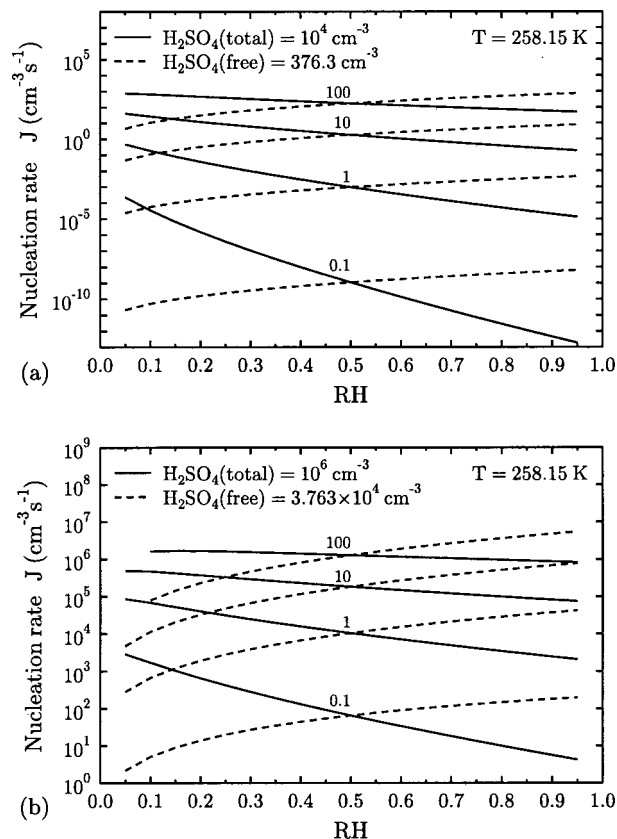


FIG. 8. Nucleation rate as a function of relative humidity at $T = 258.15 \text{ K}$. Total sulfuric acid concentration is (a) 10^4 cm^{-3} and (b) 10^6 cm^{-3} . Behavior with constant total and free sulfuric acid are compared. Ammonia mixing ratio (in ppt) is indicated for each pair of curves.

because the water activity in the corresponding vapor is outside the range of validity of the thermodynamic model.

Figure 2 presents nucleation rate as a function H_2SO_4 concentration for four different NH_3 mixing ratios and two temperatures at $\text{RH} = 50\%$. A related plot is shown in Fig. 3 which depicts nucleation rate as a function of NH_3 mixing ratio. Ammonia seems to have a twofold effect on nucleation rates. It is clearly evident that an increase of one order of magnitude in ammonia mixing ratio can increase nucleation rate several orders of magnitude (see also Fig. 1 for a comparison with the binary $\text{H}_2\text{O-H}_2\text{SO}_4$ limit). This effect is most pronounced at high temperatures and low H_2SO_4 concentrations. On the other hand, increasing H_2SO_4 concentration results in smaller enhancement of nucleation if the background NH_3 concentration is high. These observations imply that the mole fractions of NH_3 (or H_2SO_4) in the liquid phase reach their highest possible values at low temperatures and nucleation rates are less affected by a further increase in trace gas concentrations.

A related phenomenon is seen in Fig. 4 which depicts the temperature dependency of nucleation rate. Decreasing temperature at constant H_2SO_4 and NH_3 concentrations nucleation rate first increases steeply, then reaches a plateau at about 250 K, after which no significant change is seen. This limit is almost independent of the given H_2SO_4 and NH_3 concentrations.

The bulk composition and the total number of molecules

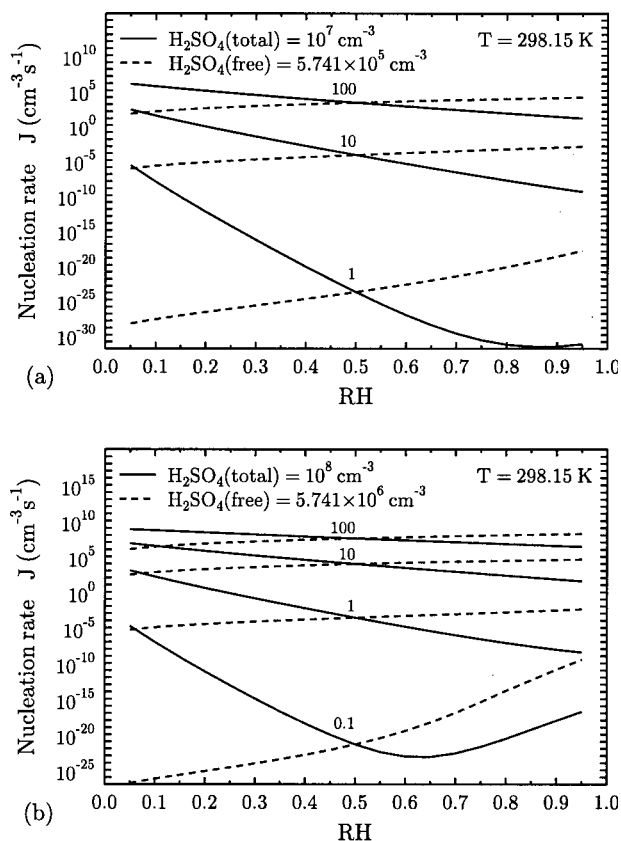


FIG. 9. Same as Fig. 6 but at $T=298.15$ K. Total sulfuric acid concentration is (a) 10^7 cm^{-3} , (b) 10^8 cm^{-3} .

in the critical nuclei as a function of temperature are shown in Figs. 5 and 6, respectively. The ambient gas concentrations correspond to the dotted curves of Fig. 4. It can be seen from Fig. 5 that the upper limit of the mole fraction of H_2SO_4 is attained at about 270 K, whereas the mole fraction of NH_3 increases up to the lowest temperatures. Increasing the vapor concentration of NH_3 results in higher mole fractions of both H_2SO_4 and NH_3 in a critical cluster at high temperatures, but at low temperatures the effect on the mole fraction of H_2SO_4 is reversed. This reflects the fact that the clusters below 280 K are practically devoid of water and, thus, the mole fractions of H_2SO_4 and NH_3 are directly coupled. Comparing Fig. 6 with Fig. 4 shows that the clusters responsible for nucleation rates higher than $1 \text{ cm}^{-3} \text{ s}^{-1}$ contain only few molecules. This indicates transition from the nucleation regime to barrierless growth of particles, which, in turn, seems to be connected with the aforementioned limiting behavior in Fig. 4.

Figure 7 shows the vapor concentrations needed to produce nucleation rate $1 \text{ cm}^{-3} \text{ s}^{-1}$ at temperatures 258.15 K, 278.15 K, and 298.15 K. Also shown here are model calculations from Korhonen *et al.*¹³ at 278.15 K and 298.15 K (Fig. 4 of Ref. 13), which are not based on the thermodynamic model of Clegg. Although both the models result in an almost linear relationship between the logarithmic concentrations of H_2SO_4 and NH_3 , the slopes of the lines are quite different. The new calculations also suggest stronger temperature dependence. At $T=298.15$ K the models almost agree (perhaps coincidentally) in the atmo-

spherically most relevant range of sulfuric acid concentrations (10^6 – 10^7 cm^{-3}) but, according to the present model, much lower ammonia concentrations are required at $T=278.15$ K.

The effect of hydration becomes most evident in Figs. 8 and 9, which show nucleation rate as a function of relative humidity for different combinations of temperature and vapor concentrations of H_2SO_4 and NH_3 . Curves of constant total H_2SO_4 and free H_2SO_4 are shown in each figure. The values of free H_2SO_4 are adjusted so that the curves intersect at $RH=50\%$. The curves corresponding constant total H_2SO_4 (solid lines) may seem contradictory: nucleation rate decreases with increasing water content in the vapor. However, the constant free H_2SO_4 curves show the expected upward slope, which indicates that hydration consumes free H_2SO_4 to the extent that nucleation slows regardless of increasing RH . This effect is more pronounced at low NH_3 concentrations. Nucleation rate seems to be less dependent on RH at low temperatures and high trace gas concentrations, which is not surprising since the corresponding critical clusters are almost water-free.

Interestingly, the curve for 0.1 ppt of NH_3 in Fig. 9(b) shows an inverted trend at $RH>60\%$. We believe, however, that this is an artifact arising from classical nucleation theory, because the critical clusters corresponding to this part of the curve are beginning to lose their H_2SO_4 and NH_3 content, which, in view of the discussion in the previous section, makes the results doubtful. A similar problem is also seen in the 1 ppt curve in Fig. 9(a). We do not consider this as a serious restriction to the practical application of the present model because the unexpected behavior seems to be limited to very low nucleation rates.

IV. DISCUSSION AND CONCLUSIONS

In this study, we have presented a revised model of ternary H_2O – H_2SO_4 – NH_3 nucleation. The model calculations encompass a wider range of atmospherically relevant conditions than our previous models. The equilibrium vapor pressures are now in an experimentally sound basis and the kinetic prefactor of nucleation rate is calculated rigorously. Furthermore, the equilibrium size distribution of clusters is replaced with a self-consistent version which obeys the law of mass action.

Superficially, most of the new results are in accord with earlier results, and we can still safely conclude that the presence of ammonia in the atmosphere increases homogeneous nucleation rates by several orders of magnitude; this effect, however, diminishes drastically at low temperatures. The dependence on H_2SO_4 and NH_3 concentrations is quite different in the new model, although at $T=298$ K and at medium sulfuric acid concentrations a fair agreement is found. Also, the hydration correction causes a definite dependence on RH , whereas the old model suggested that nucleation rate is almost independent on RH .

The clusters required to achieve significant nucleation rates are very small, containing usually less than ten molecules and almost no water. We also found that the clusters corresponding to the same constant nucleation rate are

smaller and more concentrated in H_2SO_4 and NH_3 at low temperatures, where even modest concentrations of trace gases seem to lead to barrierless nucleation. One should, however, bear in mind that at low temperatures the solution may exist in solid form and the thermodynamical model is thus unable to describe the behavior of liquid droplets.

The validity of the model is further restricted by the well-known shortcomings of classical nucleation theory which necessitates a critical examination of the results. Also, the present fits for liquid density and surface tension can only be considered as provisional. It seems that the model is especially unsuitable to cases where the critical droplets contain comparable amounts of H_2O , H_2SO_4 , and NH_3 ; luckily, these clusters are related to very low nucleation rates. On the other hand, the very small clusters at high nucleation rates cannot be dealt with properly within the limits of capillarity approximation. However, in the absence of comprehensive and reliable measurements of nucleation in $\text{H}_2\text{O-H}_2\text{SO}_4\text{-NH}_3$ vapors, no definite judgment on the reliability of the model can be made. In spite of these deficiencies, we are confident that the calculated nucleation rates are correct enough to allow successful implementation in atmospheric models.

ACKNOWLEDGMENTS

We thank Dr. Simon Clegg for his help concerning the thermodynamical code. This work was supported by the Academy of Finland (Project No. 47668), Maj and Tor Nessling Foundation, and the Estonian Science Foundation (Grant No. 3903).

- ¹R. J. Weber *et al.*, *Geophys. Res. Lett.* **26**, 307 (1999).
- ²M. Kulmala, L. Pirjola, and J. M. Mäkelä, *Nature (London)* **404**, 66 (2000).
- ³M. Kulmala, A. Laaksonen, and L. Pirjola, *J. Geophys. Res.* **103**, 8301 (1998).
- ⁴J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (Wiley, New York, 1998).
- ⁵D. S. Covert, V. N. Kapustin, P. K. Quinn, and T. S. Bates, *J. Geophys. Res.* **97**, 20581 (1992).
- ⁶W. A. Hoppel, G. M. Frick, J. W. Fitzgerald, and R. E. Larson, *J. Geophys. Res.* **99**, 14443 (1994).
- ⁷C. O'Dowd *et al.*, *Geophys. Res. Lett.* **26**, 1707 (1999).
- ⁸J. M. Mäkelä *et al.*, *Geophys. Res. Lett.* **24**, 1219 (1997).
- ⁹R. C. Easter and R. K. Peters, *J. Appl. Meteorol.* **33**, 775 (1994).
- ¹⁰E. Nilsson and M. Kulmala, *J. Geophys. Res.* **103**, 1381 (1998).
- ¹¹W. D. Scott and F. C. R. Cattell, *Atmos. Environ.* **13**, 307 (1979).
- ¹²D. J. Coffman and D. A. Hegg, *J. Geophys. Res.* **100**, 7147 (1995).
- ¹³P. Korhonen *et al.*, *J. Geophys. Res.* **104**, 26349 (1999).
- ¹⁴S. M. Ball, D. R. Hanson, and F. L. Eisele, *J. Geophys. Res.* **104**, 23709 (1999).
- ¹⁵M. Kulmala *et al.*, *J. Geophys. Res.* (accepted).
- ¹⁶S. L. Clegg, P. Brimblecombe, and A. S. Wexler, *J. Phys. Chem. A* **102**, 2137 (1998).
- ¹⁷M. Noppel, H. Vehkamäki, and M. Kulmala, *J. Chem. Phys.* **116**, 218 (2002).
- ¹⁸A. Laaksonen, R. McGraw, and H. Vehkamäki, *J. Chem. Phys.* **111**, 2019 (1999).
- ¹⁹G. P. Ayers, R. W. Gillett, and J. L. Gras, *Geophys. Res. Lett.* **7**, 433 (1980).
- ²⁰M. Kulmala and A. Laaksonen, *J. Chem. Phys.* **93**, 696 (1990).
- ²¹J. Marti *et al.*, *J. Geophys. Res.* **102**, 3725 (1997).
- ²²R. Van Dingenen and F. Raes, *J. Aerosol Sci.* **24**, 1 (1993).
- ²³H. Arstila, P. Korhonen, and M. Kulmala, *J. Aerosol Sci.* **30**, 131 (1999).
- ²⁴H. Trinkhaus, *Phys. Rev. B* **27**, 7372 (1983).
- ²⁵K. Binder and D. Stauffer, *Adv. Phys.* **25**, 343 (1976).
- ²⁶M. Noppel, in *Nucleation and atmospheric aerosols 2000. 15th International Conference*, edited by B. Hale and M. Kulmala (AIP conference proceedings, Melville, New York, 2000), Vol. 534, pp. 339–342.
- ²⁷H. Reiss, *J. Chem. Phys.* **18**, 840 (1950).
- ²⁸G. Wilemski and B. E. Wyslouzil, *J. Chem. Phys.* **103**, 1127 (1995).
- ²⁹I. Napari and A. Laaksonen, *J. Phys. Chem. B* **105**, 11678 (2001).