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Ternary nucleation of H_2SO_4, NH_3, and H_2O in the atmosphere

P. Korhonen,[1,2] M. Kulmala,[1] A. Laaksonen,[3] Y. Viisanen,[2]
R. McGraw,[4] and J. H. Seinfeld[5]

Abstract. Classical theory of binary homogeneous nucleation is extended to the ternary system H_2SO_4-NH_3-H_2O. For NH_3 mixing ratios exceeding about 1 ppt, the presence of NH_3 enhances the binary H_2SO_4-H_2O nucleation rate by several orders of magnitude. The Gibbs free energies of formation of the critical H_2SO_4-NH_3-H_2O cluster, as calculated by two independent approaches, are in substantial agreement. The finding that the H_2SO_4-NH_3-H_2O ternary nucleation rate is independent of relative humidity over a large range of H_2SO_4 concentrations has wide atmospheric consequences. The limiting component for ternary H_2SO_4-NH_3-H_2O nucleation is, as in the binary H_2SO_4-H_2O case, H_2SO_4; however, the H_2SO_4 concentration needed to achieve significant nucleation rates is several orders of magnitude below that required in the binary case.

1. Introduction

Binary, homogeneous nucleation of H_2SO_4 and H_2O has for some time been presumed to be the principal mechanism for new particle formation in the atmosphere [*Hegg et al.*, 1990; *Clarke*, 1992, 1993; *Eisele and Tanner*, 1993; *Perry and Hobbs*, 1994; *Raes and Van Dingenen*, 1992; *Raes et al.*, 1993; *Pandis et al.*, 1994; *Russell et al.*, 1994; *Raes*, 1995; *Weber et al.*, 1995, 1996, 1997, 1999; *Weber and McMurry*, 1996; *Kulmala et al.*, 1995; *Andronache et al.*, 1997; *Pirjola et al.*, 1998]. With the advent of means to measure H_2SO_4 vapor and ultrafine particle concentrations simultaneously, it has become possible to evaluate observed atmospheric new particle formation rates with those predicted by nucleation theories. While several studies show that measured new particle formation rates, such as in the upper troposphere, are consistent with those predicted to occur by binary nucleation of H_2SO_4 and H_2O [*Clarke et al.*, 1999; *Weber et al.*, 1999], others, especially those in the marine boundary layer or over continental sites, indicate that observed ambient nucleation rates substantially exceed those predicted based on binary H_2SO_4-H_2O nucleation [*Covert et al.*, 1992; *Weber et al.*, 1996, 1997, 1998, 1999; *Clarke et al.*, 1998]. One explanation for this discrepancy is the participation of a third molecule, and the species considered to be most likely is NH_3, which is ubiquitous in the atmosphere. Because the presence of NH_3 in the particles considerably decreases the vapor pressure of H_2SO_4 above the solution [e.g., *Scott and Cattell*, 1979], NH_3 is expected to facilitate the nucleation of H_2SO_4-H_2O [*Coffman and Hegg*, 1995].

In this paper, we present a classical theory of the ternary nucleation of H_2SO_4-NH_3-H_2O. We compare predicted rates of nucleation in the ternary system to those of the binary H_2SO_4-H_2O system at atmospheric levels of H_2SO_4 and NH_3. One caution should be noted in regard to this and other treatments of nucleation based on the classical theory. Whereas some laboratory nucleation rate measurements do not agree with classical theory predictions, others do; for example, the recent parameterization of H_2SO_4-H_2O nucleation theory [*Kulmala et al.*, 1998] agrees with laboratory measurements of *Viisanen et al.* [1997]. Although molecular-based theories that address limitations of classical theory are a subject of current attention [*Kusaka et al.*, 1998], at present a predictive molecular theory of binary nucleation does not exist. Thus a classical theory still represents the standard for atmospheric application and that against which molecular theories will ultimately be compared.

2. Theory of Ternary Nucleation

The ternary H_2SO_4-NH_3-H_2O nuclei are assumed to be in the liquid phase. The rate of nucleation of stable ternary clusters is given by

$$J = C\exp\left(-\frac{\Delta G^*}{kT}\right) \tag{1}$$

where ΔG^* is the free energy of formation of the critical cluster and C is a kinetic factor. ΔG^* is determined here using the so-called revised classical theory

$$\Delta G^* = \frac{4}{3}\pi r^{*2}\sigma \tag{2}$$

where r^* is the radius of the critical cluster and σ is the surface tension. The composition of the critical nucleus is obtained from [*Arstila et al.*, 1999],

[1] Department of Physics, University of Helsinki, Helsinki, Finland.
[2] Air Quality Research, Finnish Meteorological Institute, Helsinki, Finland.
[3] Department of Applied Physics, University of Kuopio, Kuopio, Finland.
[4] Environmental Chemistry Division, Brookhaven National Laboratory, Upton, New York.
[5] Division of Engineering and Applied Science and Department of Chemical Engineering, California Institute of Technology, Pasadena.

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$$-kT\ln\left(\frac{p_1}{p_{s,1}}\right)+\frac{2\sigma v_1}{r}=-kT\ln\left(\frac{p_2}{p_{s,2}}\right)+\frac{2\sigma v_2}{r}=-kT\ln\left(\frac{p_i}{p_{s,i}}\right)+\frac{2\sigma v_i}{r} \quad (3)$$

where p_i is the ambient partial pressure 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 cluster, and v_i is the partial molecular volume of species i.

For a critical cluster of H_2SO_4-NH_3-H_2O, equation (3) becomes

$$\nu_{H_2SO_4}\ln\left(\frac{p_{H_2O}}{p_{s,H_2O}}\right)-\nu_{H_2O}\ln\left(\frac{p_{H_2SO_4}}{p_{s,H_2SO_4}}\right)=0$$
$$\nu_{NH_3}\ln\left(\frac{p_{H_2O}}{p_{s,H_2O}}\right)-\nu_{H_2O}\ln\left(\frac{p_{NH_3}}{p_{s,NH_3}}\right)=0 \quad (4)$$

The composition of the critical cluster can be obtained from equations (4) by numerical iteration. When the composition is known, the radius of the critical cluster is obtained from the Kelvin equation,

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

In this context, i refers to either H_2SO_4, NH_3, or H_2O. The rigorous kinetic factor C for a ternary system, used also in the current study, was obtained by *Arstila et al.* [1999].

3. Thermodynamic Models

To determine the radius and composition of the critical cluster, one needs surface tension (surface free energy), solution density, and equilibrium vapor pressures of the various species above the flat solution surface. When classical nucleation theory is used, the thermodynamic properties of the nucleus are assumed to be those of the corresponding bulk solution [*Korhonen et al.*, 1998a].

The required vapor pressures of H_2SO_4, NH_3, and H_2O above the flat solution surface are obtained from [*Bassett and Seinfeld*, 1983; *Kim et al.*, 1993],

$$p_{s,H_2SO_4}=\frac{\gamma^3_{2H,SO_4}m_H^2m_{SO_4}}{K_{H_2SO_4}} \quad (6)$$

$$p_{s,NH_3}=\frac{\gamma^2_{NH_4,OH}m_{NH_4}m_{OH}}{K_{NH_3}K_{NH_4}a_{H_2O}} \quad (7)$$

$$p_{s,H_2O}=a_{H_2O}p_{e,H_2O} \quad (8)$$

where m_i is the molality (mol per kg of pure water) of species i, $\gamma_{i,j}$ is the mean molal activity coefficient of ion pair i,j in the multicomponent solution [see, e.g., *Bassett and Seinfeld*, 1983], a_{H_2O} is the (liquid phase) activity of H_2O, p_{e,H_2O} is the equilibrium vapor pressure of water above a flat surface of pure water, and K_i are thermodynamic equilibrium constants for dissociation. The subscript H refers to hydrogen ion (H^+), SO_4 refers to sulfate ion (SO_4^{2-}) NH_4 refers to ammonium ion (NH_4^+) and OH refers to hydroxyl ion (OH^-).

In aqueous solution, H_2SO_4 molecules undergo two dissociation steps:

$$H_2SO_4(aq)\leftrightarrow H^++HSO_4^-$$

$$HSO_4^-\leftrightarrow H^++SO_4^{2-}$$

The first dissociation is assumed here to be essentially complete. The extent of the second dissociation is described by [*Bassett and Seinfeld*, 1983; *Clegg et al.*, 1994],

$$\frac{\gamma_H\gamma_{SO_4}m_Hm_{SO_4}}{\gamma_{HSO_4}m_{HSO_4}}=\frac{\gamma^3_{2H,SO_4}m_Hm_{SO_4}}{\gamma^2_{H,HSO_4}m_{HSO_4}}=K_{HSO_4} \quad (9)$$

where γ_i is the molal activity coefficient of ion species i. Let $\alpha=m_{SO_4}/m_{H_2SO_4}$ be the degree of bisulfate dissociation. The concentrations of bisulfate, sulfate, and hydroxyl ions can then be determined from

$$m_{HSO_4}=(1-\alpha)m_{H_2SO_4} \quad (10)$$

$$m_{SO_4}=\alpha m_{H_2SO_4} \quad (11)$$

$$m_{OH}=\frac{K_{H_2O}a_{H_2O}}{\gamma^2_{H,OH}m_H} \quad (12)$$

where K_{H_2O} is the equilibrium constant for the dissociation $H_2O(aq)\leftrightarrow H^++OH^-$.

We must calculate NH_4^+ concentration in solutions ranging from acidic to alkaline. In acidic solution, sufficient H^+ ions exist to transform practically every NH_3 molecule to NH_4^+. In alkaline solution, however, a considerable amount of $NH_3(aq)$ can be present. Let m^o_{NH} be the total amount of ammonium species (NH_3 plus NH_4^+) in the solution,

$$m^o_{NH}=m_{NH_3}+m_{NH_4} \quad (13)$$

We obtain the concentration of NH_4^+ ions by combining this relation with the equilibrium relation for $NH_3(aq)+H_2O(aq)\leftrightarrow NH_4^++OH^-$. The result is

$$K_{NH_4}=\frac{\gamma^2_{NH_4,OH}m_{NH_4}m_{OH}}{\gamma_{NH_3}m_{NH_3}a_{H_2O}}=\frac{\gamma^2_{NH_4,OH}m_{NH_4}K_{H_2O}}{\gamma_{NH_3}m_{NH_3}\gamma^2_{H,OH}m_H} \quad (14)$$

where γ_{NH_3} is the activity coefficient for NH_3(aq). To obtain the last term on the right hand side of equation (14), we have used the water equilibrium. From equations (13) and (14), we obtain

$$m_{NH_4} = \frac{m^o_{NH}}{\left(1 + \frac{\gamma^2_{NH_4,OH} K_{H_2O}}{\gamma^2_{H,OH}\gamma_{NH_3} K_{NH_4} m_H}\right)} \tag{15}$$

The above equations for the ion concentrations depend on the H^+ concentration, activity coefficients, and thermodynamic equilibrium constants. The H^+ concentration is obtained by numerical iteration with the electroneutrality relation,

$$m_H + m_{NH_4} - m_{HSO_4} - 2m_{SO_4} - m_{OH} = 0 \tag{16}$$

The required mean molal activity coefficients for the multicomponent solution are calculated using the mixing rule of *Kusik and Meissner* [1978]. The water activity for the multicomponent ionic solution is determined by [*Stelson et al.*, 1984],

$$\begin{aligned}\ln a'_{H_2O} = &\sum_{ij} \frac{\nu_{ij} m_{ij} z_i z_j}{I(z_i + z_j)} \left[z_j \sum_k \left(\frac{z_i + z_k}{2}\right)^2 \ln a^o_{H_2O,k} \right. \\ &\left. + z_i \sum_l \left(\frac{z_l + z_j}{2}\right)^2 \ln a^o_{H_2O,l} \right] \\ &+ \frac{M_{H_2O}}{10^3} \sum_{ij} \left[\frac{\nu_{ij} m_{ij}}{(z_i + z_j)} \left\{ z_i \left[\sum_k \left(\frac{z_i + z_k}{2}\right)^2 \frac{m_k}{I} - 1 \right] \right.\right. \\ &\left.\left. + z_j \left[\sum_l \left(\frac{z_l + z_j}{2}\right)^2 \frac{m_l}{I} - 1 \right] \right\} \right]\end{aligned} \tag{17}$$

Because, in some cases, there may exist a considerable amount of ammonia in solution, an effect that equation (11) does not account for, we use the approach of *Stelson et al.* [1984] for the unreactive solute. From the Gibbs-Duhem equation one can obtain water activity for a solution containing ionic solutes and unreactive solute, which in this case is NH_4OH. The result is

$$a_{H_2O} = \exp(\ln a'_{H_2O} + \ln a_{H_2O,NH_4OH}) \tag{18}$$

where a_{H_2O,NH_4OH} refers to the water activity caused by the undissociated NH_4OH alone.

The critical cluster free energy ΔG^* was calculated by two approaches utilizing different sets of thermodynamic parameters (Figure 1). The curves are computed for $H_2SO_4=10^6$ molecules cm^{-3}. Between relative humidity (RH)=52.3% and 90%, the critical energy is independent of RH. The curve labeled A was computed using surface tension and density from the approach of *Van Dingenen and Raes* [1993], modified to produce the correct surface tensions in the limits of $(NH_4)_2SO_4$-H_2O and NH_4HSO_4-H_2O [*Korhonen et al.*, 1998b]. Binary solution activity coefficients and other required thermodynamic data were obtained from *International Critical Tables (ICT)* [1960], *Kim et al.* [1993], and *Clegg and Brimblecombe* [1995]. The thermodynamic constant $K_{H_2SO_4}$ in equation (6) has been chosen so that the nucleation rate for the binary system H_2SO_4-H_2O calculated with equation (6) agrees with the experimental binary nucleation rates measured by *Viisanen et al.* [1997] at 52.3% RH. The curve labeled B was calculated based on component activities estimated using the multicomponent thermodynamic model of *Clegg et al.* [1998] (www.uea.ac.uk/~e770/aim.html). To estimate the thermodynamic properties of the critical cluster, surface tension and molecular volume were estimated based on standard mixing rules applied to data available for the binary mixtures, $(NH_4)_2SO_4$-H_2O and H_2SO_4-H_2O [*Gurovich et al.*, 1983; *ICT*, 1960; *Shugard et al.*, 1974]. Both thermodynamic models lead to essentially the same value of $K_{H_2SO_4}$.

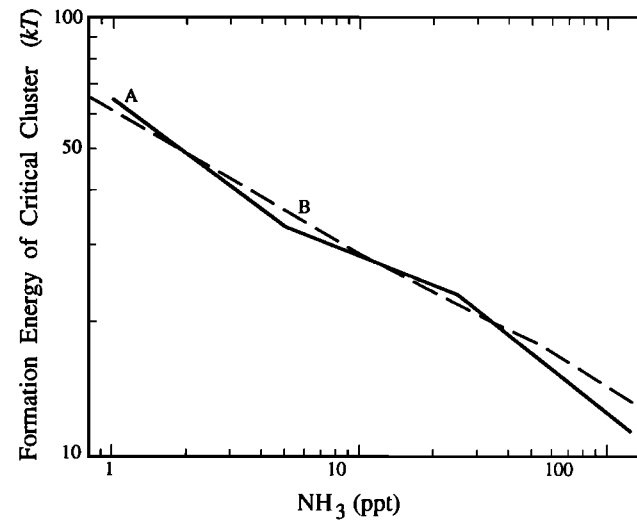

Figure 1. Critical cluster free energy for ternary H_2SO_4-NH_3-H_2O nucleation. H_2SO_4 concentration equal to 10^6 molecules cm^{-3}. Conditions of calculation of curves A and B described in text.

4. Predicted Ternary Nucleation Rates

The predicted ternary H_2SO_4-NH_3-H_2O nucleation rate is shown in Figure 2 as a function of H_2SO_4 number concentration at 90% RH and 298 K, and at NH_3 mixing ratios of 0, 1, 2, 3, 5, 7, 10, and 15 ppt. The presence of NH_3 enhances the binary nucleation rate by several orders of magnitude, as long as the NH_3 mixing ratio exceeds about 1 ppt; below 1 ppt there is little effect on the binary rate. Figure 3 presents the same results, except at 52.3% RH. This RH was chosen to correspond to that at which experimental measurements of binary H_2SO_4-H_2O nucleation were reported by *Viisanen et al.* [1997]. From both Figures 2 and 3, it is evident that after some limit increasing NH_3 concentration does not further enhance the nucleation rate. Figure 4 shows the threshold for significant nucleation, considered as that exceeding a rate of 1 cm^{-3} s^{-1}, as

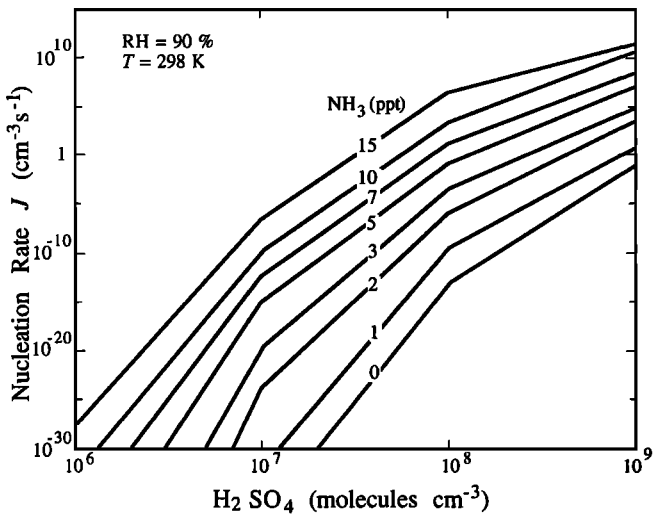

Figure 2. Predicted ternary nucleation rate at 298 K and 90% RH.

a function of H_2SO_4 and NH_3 concentrations at 298 K and 278 K. It should be noted that at this time we do not have experimental data at temperatures other than 298 K in order to obtain the correct binary nucleation limit. Thus predictions at other temperatures should be viewed as more uncertain than those at 298 K. Ternary nucleation is essentially independent of RH for H_2SO_4 concentrations less than 10^8 cm^{-3} and NH_3 mixing ratios exceeding 5 ppt. When $[H_2SO_4] > 10^7$ cm^{-3} and NH_3 mixing ratio exceeds 20 ppt, significant nucleation occurs. On the other hand, at an H_2SO_4 concentration of 10^6 molecules cm^{-3}, over 100 ppt NH_3 is needed for significant nucleation. The rates presented represent the results of more than 200 model calculations. The rates are best estimates with error bars of ±3 to 5 orders of magnitude (Figures 2 and 3). Error bars in NH_3 concentration at fixed H_2SO_4 concentration is 30 to 50% (Figure 4).

The finding that the H_2SO_4-NH_3-H_2O ternary nucleation rate is independent of RH over a wide range of H_2SO_4 concentrations has wide atmospheric consequences. The limiting component for ternary H_2SO_4-NH_3-H_2O nucleation is, as in the

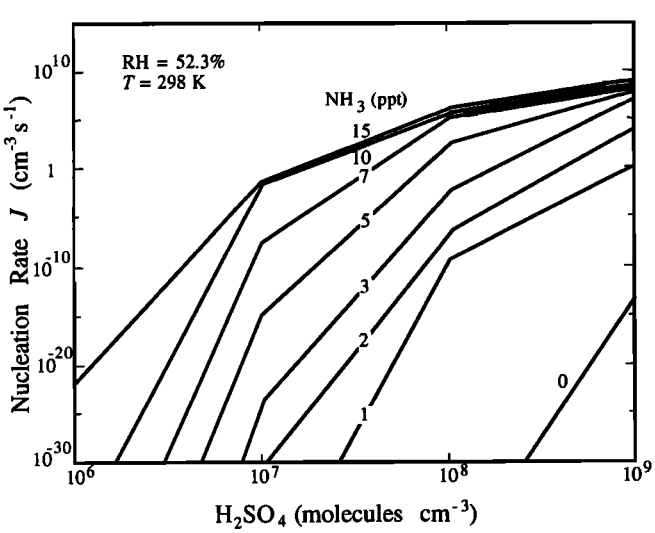

Figure 3. Predicted ternary nucleation rate at 298 K and 52.3% RH.

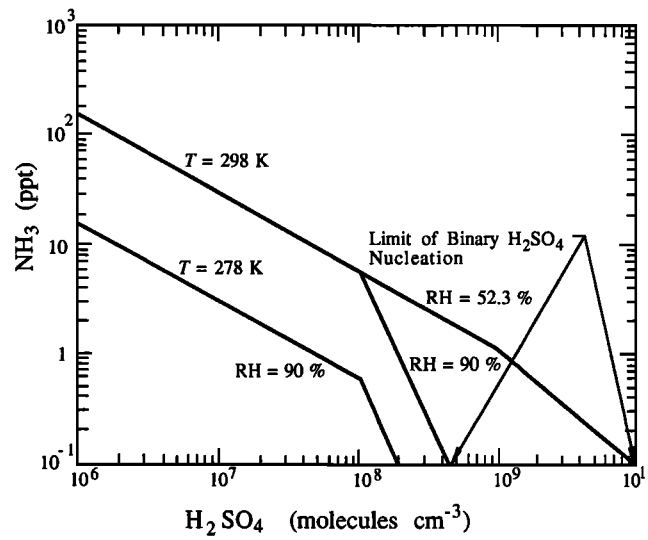

Figure 4. Threshold for significant ternary H_2SO_4-NH_3-H_2O nucleation. T=298 K and 278 K.

binary H_2SO_4-H_2O case, H_2SO_4; however, the H_2SO_4 concentration needed to achieve significant nucleation rates is several orders of magnitude below that required in the binary case. In Figure 1, the concentration of free acid molecules is fixed at 10^6 cm^{-3}; then the results are indeed independent of RH. However, for a fixed total acid (free acid plus hydrates), as the RH changes, the partitioning between free acid and hydrates will also change. So, in practice, as the RH changes, the free acid concentration will also change. We have not addressed the important question of whether in the atmosphere, for example, at fixed total acid concentration, the barrier height, and therefore nucleation rate, is indeed independent of RH. That would require invoking a hydrate model for the partitioning, which is beyond the scope of this paper. Thus the ternary nucleation rate is independent of RH for certain limits for given temperature and concentration of free acid. This finding suggests that when ternary nucleation is occurring there should not be a strong dependence on the value of RH. Whereas atmospheric measurements do indicate enhanced new particle formation in regions of high RH, there are also a variety of observations of new particle formation at low RH values [*Weber et al.*, 1999].

Some studies have suggested that observed atmospheric nucleation rates can be "barrierless," in that the rate appears to be controlled by that of monomer-monomer collision [*Weber et al.*, 1996]. While the ternary H_2SO_4-NH_3-H_2O nucleation rate is indeed significantly faster than that of binary H_2SO_4-H_2O nucleation, it is still not barrierless. For example, at 298 K and 52.3% RH, and at 5 ppt NH_3 and 10^8 molecules H_2SO_4 cm^{-3}, the critical cluster contains 18 molecules (8 H_2SO_4, 4 NH_3, 6 H_2O). (The corresponding classical binary H_2SO_4-H_2O nucleation rate under these conditions is 10^{-32} cm^{-3} s^{-1}, with a critical cluster of 130 molecules.) *Ianni and Bandy* [1999], in a theoretical study of the addition of one NH_3 molecule to sulfuric acid hydrates, also conclude that one NH_3 molecule is not able to stabilize the hydrates sufficiently to initiate aerosol formation.

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P. Korhonen and M. Kulmala, Department of Physics, University of Helsinki, P.O. Box 9, 00014 University of Helsinki, Helsinki, Finland.

A. Laaksonen, Department of Applied Physics, University of Kuopio, P.O. Box 1627, 70211 Kuopio, Finland.

R. McGraw, Environmental Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973.

J. H. Seinfeld (corresponding author), Division of Engineering and Applied Science and Department of Chemical Engineering, California Institute of Technology, Mail Code 104-44, Pasadena, CA 91125. (seinfeld@its.caltech.edu)

Y. Viisanen, Air Quality Research, Finnish Meteorological Institute, Sahaajankatu 20E, 00810 Helsinki, Finland.

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