Ternary Nucleation of H_2SO_4, NH_3 and H_2O

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Abstract. A classical theory of the ternary homogeneous nucleation of sulfuric acid – ammonia – water is presented. For NH_3 mixing ratios exceeding 1 ppt, the presence of ammonia enhances the binary (sulfuric acid –water) nucleation rate by several orders of magnitude. However, the limiting component for ternary nucleation – as for binary nucleation – is sulfuric acid. The sulfuric acid concentration needed for significant ternary nucleation is several orders of magnitude below that required in binary case.

INTRODUCTION

Water vapor is the most abundant gaseous species in the atmosphere that may take part on the new particle formation. However, for the homogenous nucleation process, in which new particles form from a single species only, its typical concentrations are far too small. Thus it is generally accepted that the new particle formation in the atmosphere occurs via homogenous heteromolecular nucleation process, in which two or more vapor species form new stable particles. In the past the atmospheric new particle formation was almost always assumed to take place via binary nucleation of water (H_2O) and sulfuric acid (H_2SO_4) vapors. Field measurements have been shown that there exists situations where the new particle formation cannot be explained with this nucleation route alone [1-3]. Although meteorological factors (e.g. mixing) may play an important role in some cases, researchers have begun to search for additional mechanisms that may launch nucleation in the atmospheric conditions. Because the presence of ammonia in the aerosol particles considerably decreases the vapor pressure of sulfuric acid above the solution surface [4], it has been suggested, that ammonia (NH_3) forms new particles with sulfuric acid [4] or with sulfuric acid and water [5].

We have recently shown theoretically [6] that ternary nucleation is important phenomena in the atmosphere. Its importance in aerosol dynamics point of view have also been studied [7]. In this paper we apply the ternary nucleation model on atmospheric conditions. We also summarize the ternary nucleation theory and also the thermodynamics used.

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THEORY FOR THE TERNARY NUCLEATION

In the following we focus on the formation of new particles via nucleation of stable H_2O - NH_3 - H_2SO_4 clusters. The ternary water - ammonia - sulfuric acid solution nuclei are assumed to be in the liquid phase. The nucleation rate of stable water-ammonia- sulfuric acid clusters (J) is obtained from

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

Here C is a kinetic factor. In this study the minimum work for the critical nucleus formation is determined using the so called revised classical theory. The minimized Gibbs free energy change (in the limits of capillarity approximation) is obtained from

$$\Delta G^* = \frac{4}{3}\pi r^{*2}\,\sigma_{s/a} \tag{2}$$

where r^* is the critical radius of the cluster and $\sigma_{s/a}$ is the surface tension. The critical nucleus composition is obtained from the following equations (Arstila *et al.*, 1998):

$$-kT\ln\left(\frac{P_1}{P_{s,1}}\right)+\frac{2\sigma_{s/a}v_1}{r} = -kT\ln\left(\frac{P_2}{P_{s,2}}\right)+\frac{2\sigma_{s/a}v_2}{r} =\ldots= -kT\ln\left(\frac{P_i}{P_{s,i}}\right)+\frac{2\sigma_{s/a}v_i}{r} = 0 \tag{3}$$

where P_i is the ambient partial vapor pressure of species i, $P_{s,i}$ is the equilibrium vapor pressure of species i above the flat solution surface, r is the radius of the cluster and v_i is the partial molecular volume of species i.
When the critical cluster is formed from water, ammonia and sulfuric acid equation (3) becomes:

$$\begin{aligned} v_{h2so4}\ln\left(\frac{P_w}{P_{s,w}}\right) - v_w\ln\left(\frac{P_{h2so4}}{P_{s,h2so4}}\right) &= 0 \\ v_{nh3}\ln\left(\frac{P_w}{P_{s,w}}\right) - v_w\ln\left(\frac{P_{nh3}}{P_{s,nh3}}\right) &= 0 \end{aligned} \tag{4}$$

Here subscript w refers to water, *h2so4* to sulfuric acid and *nh3* to ammonia. From equations (4) one can solve the composition of the critical cluster by numerical iteration. When the composition of the cluster is known, the critical radius is obtained from the Kelvin equation

$$r^* = \frac{2\sigma_{s/a}v_i}{kT\ln\left(\frac{P_i}{P_{s,i}}\right)} \tag{5}$$

In this context i refers either water or ammonia or sulfuric acid. We have used recently presented rigorous kinetic factor for the ternary system [8]. In order to solve the radius and composition of the critical cluster for the systems presented above, one needs surface tension (surface free energy), density of the solution and equilibrium vapor pressures of the various species above the flat solution surface. When the classical nucleation theory is used, the thermodynamical properties of the nucleus are assumed to be those of bulk substance in question. Our recent paper [6] summarizes the thermodynamical model.

RESULTS AND DISCUSSION

According to the present knowledge, the nucleation of new aerosol particles in the atmospheric conditions in significant extent can occur The results of this model study suggest that nucleation of water – ammonia - sulfuric acid clusters occurs easier than the nucleation of water – sulfuric acid clusters in the atmospheric conditions. The results also suggest that the composition of the critical clusters in the atmospheric conditions is typically that of water - ammonium bisulfate solution. However, the formed H_2O - NH_3 - H_2SO_4 clusters are very small and highly concentrated: in this study they appear to be supersaturated with respect to ammonium sulfate almost in every case we have studied [6].

The nucleation rate is a strong function of sulfuric acid concentration, ammonia concentration and temperature. In Figure 1 the ternary nucleation rate as a function of temperature is presented. Sulfuric acid concentration is $1x10^6$ cm^{-3} and ammonia concentration 25 pptv. In Figure 2 the ternary nucleation rate as a function of ammonia concentration is presented. Sulfuric acid concentration is $1x10^5$ cm^{-3} and temperature 278.15 K.

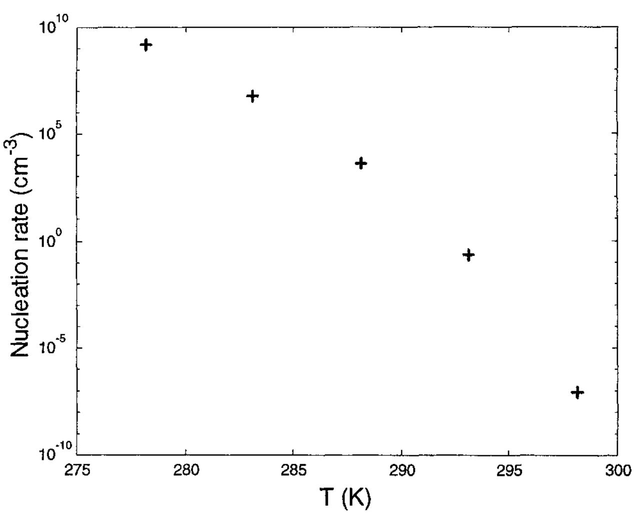

FIGURE 1. Ternary nucleation rate as a function of temperature. Sulfuric acid concentration is $1x10^6$ cm^{-3} and ammonia concentration 25 pptv.

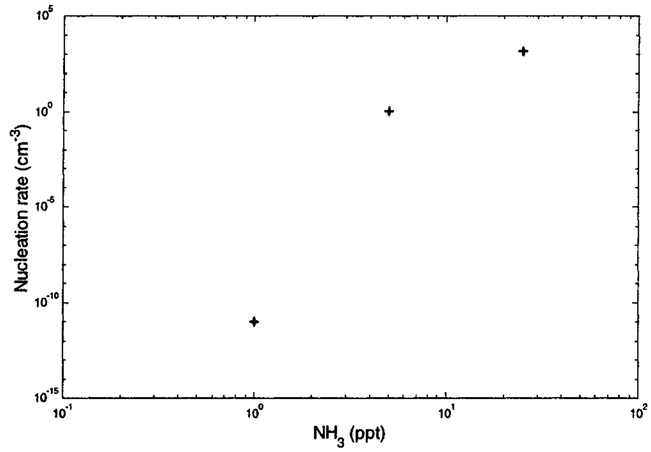

FIGURE 2. Nucleation rate as a function of ammonia concentration. Sulfuric acid concentration is $1x10^5$ cm^{-3} and temperature 278.15 K.

Although the ternary nucleation is able to predict the formation of new 1 nm particles, it is not able to predict the formation of 3 nm particles. This is due to the fact that the sulfuric acid concentration needed in ternary nucleation is too small to be able to explain the growth of 1 nm particles to 3 nm size [7], and some other vapours are needed for condensation growth.

REFERENCES

1. Covert D.S., Kapustin V.N., Quinn P.K. and Bates T.S., New Particle Formation in the Marine Boundary Layer. J. Geophys. Res., 97, 20581-20589 (1992).
2. Hoppel W.A., Frick G.M. and Fitzgerald J.W., Marine boundary layer measurements of new particle formation and the effects nonprecipating clouds have on aerosol size distribution. J. Geophys. Res., 99, 14443-14495 (1994).
3. Mäkelä J.M., Aalto P., Jokinen V., Pohja T., Nissinen A., Palmroth S., Markkanen T., Seitsonen K., Lihavainen H., Kulmala M., Observations of ultrafine aerosol particle formation and growth in boreal forest. Geophys. Res. Lett., 1219-1222 (1997).
4. Scott W.D. and Cattell F.C.R., Vapor pressure of ammonium sulfates. Atmos. Env., 13, 307-317 (1979).
5. Coffmann D.J. and Hegg. D.A., A Preliminary study of the effect of ammonia on particle nucleation in the marine boundary layer. J. Geophys. Res., 100, 7147-7160 (1995).
6. KorhonenP., Kulmala M., Laaksonen A., Viisanen Y., McGraw R., Seinfeld J.H., Ternary nucleation of H_2SO_4, NH_3 and H_2O in the atmosphere. J. Geophys. Res., 104, 26349-26353 (1999).
7. Kulmala M., Pirjola L., Mäkelä J.M., Stable sulphate clusters as a source of new atmsopheric particles. Nature, 404, 66-69 (2000).
8. Arstila H., Korhonen P. and Kulmala M., Ternary Nucleation: Kinetics and application to water - ammonia - hydrochlorid acid system. Technical note, J. Aerosol Sci. 30, 131-138 (1999).