Atmos. Chem. Phys., 6, 787–793, 2006
www.atmos-chem-phys.net/6/787/2006/

Atmospheric
Chemistry
and Physics

Cluster activation theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulphuric acid concentration

M. Kulmala[1], **K. E. J. Lehtinen**[2], **and A. Laaksonen**[3]

[1]University of Helsinki, Department of Physical Sciences, P.O. Box 64, FIN-00014 Helsinki, Finland
[2]Finnish Meteorological Institute and University of Kuopio, Department of Applied Physics, P.O.Box 1627, FIN-70211 Kuopio, Finland
[3]University of Kuopio, Department of Applied Physics, P.O.Box 1627, FIN-70211 Kuopio, Finland

Received: 7 October 2005 – Published in Atmos. Chem. Phys. Discuss.: 8 November 2005
Revised: 16 January 2006 – Accepted: 23 January 2006 – Published: 10 March 2006

Abstract. According to atmospheric observations new particle formation seems to be a function of sulphuric acid concentration to the power from one to two. The nucleation theorem then predicts that the critical cluster contains one to two sulphuric acid molecules. However, existing nucleation theories predicts that the power is more (or equal) than 2. Here we present an activation theory, which can explain the observed slope. In cluster activation the clusters containing one sulphuric acid molecule will activate for further growth due to heterogeneous nucleation, heterogeneous chemical reactions including polymerization or activation of soluble clusters. In the activation process organic vapours are typically needed as condensing agents.

1 Introduction

Aerosol particles are ubiquitous in the Earth's atmosphere and affect our quality of life in many different ways. In polluted urban environments, aerosol emissions can affect human health through their inhalation (e.g. Donaldson et al., 1998), whilst globally, aerosols are thought to contribute to climate change patterns (e.g. Charlson et al., 1987; Lohmann and Feichter, 2005). In recent years, considerable effort has been devoted to understanding how aerosols directly affect the Earth's radiation budget by scattering and absorbing incoming solar radiation. Aerosols also affect the radiation budget indirectly by modifying many cloud properties such as their albedo and lifetime. It is generally thought that increases in aerosol concentrations will lead to brighter and more sustained clouds, thus providing additional planetary cooling.

In order to be able to better understand the health and climatic effects of atmospheric aerosols, the formation and growth processes of atmospheric aerosols should also be better understood (Kulmala, 2003). Nucleation, the formation of ultrafine particles detected at a few nm, and subsequent growth to ∼100 nm in 1–2 days, has been observed frequently in the continental boundary layer. Such observations span from northern-most sub-arctic Lapland (Vehkamäki et al., 2004), over the remote boreal forest (Mäkelä et al., 1997; Kulmala et al., 1998, 2001a) and suburban Helsinki (Väkevä et al, 2000), to industrialised agricultural regions in Germany (Birmili and Wiedensohler, 1998; Laaksonen et al., 2005), coastal environments around Europe (O'Dowd et al., 1999) and Asian megacities (Mönkkönen et al., 2005). The atmospheric new particle formation rates have also been investigated by Weber et al. (1996, 1997), and the biogenic aerosol formation by Kavouras et al. (1998). A recent overview summarised the formation and growth properties in a global point of view (Kulmala et al., 2004a), quantifying especially the formation and growth rates of nucleation events where available.

It has been proposed and also observed that atmospheric new particle formation depends on the sulphuric acid concentration. In laboratory experiments this dependence is clear and straightforward (Viisanen et al., 1997; Bernd et al., 2005), and the dependence is strong, in power-law form having exponents of order 5–10. In atmospheric conditions the dependence is much smoother. In the present paper we investigate the theoretical background of the observed sulphuric acid concentration dependence. For this purpose, we derive a theory for cluster activation, and compare its predictions with kinetic nucleation and observed particle formation.

Correspondence to: M. Kulmala
(markku.kulmala@helsinki.fi)

Published by Copernicus GmbH on behalf of the European Geosciences Union.

2 Relations between fresh particle formation rate and sulphuric acid concentration

Critical clusters – if electrically neutral – formed by atmospheric nucleation events cannot yet be measured quantitatively due to instrumental limitations. Only one measurement of clusters during nucleation events has been reported, and it showed that clusters were present when 2.7–4 nm particles were detected (Weber et al., 1995). More work on the distribution and composition of such clusters is needed to refine our understanding of atmospheric nucleation. However, ion clusters can be and have been measured during nucleation events (e.g. Hörrak, 2001; Laakso et al., 2004)

Because critical neutral clusters cannot yet be measured, we are unable to measure the true atmospheric nucleation rate but rather the formation rate of particles of some larger diameter d_p. The diameter d_p corresponds typically to the CPC (condensation particle counter) detection limit, which is presently 3 nm or greater. In any case, based on the observed formation rates, the nucleation rate (formation rate of 1 nm particles) can be estimated based on theory describing the competition between condensation growth and cluster scavenging (Kerminen and Kulmala, 2002).

Using the observed nucleation mode growth rate and condensation sink determined from size spectra measurements, the concentration of condensable vapour and its source rate during the nucleation and growth events can be analysed (see Kulmala et al., 2001b; Dal Maso et al., 2002). The aerosol condensation sink determines how rapidly molecules will condense onto pre-existing aerosols and depends strongly on the shape of the size distribution (see e.g. Pirjola et al., 1999; Kulmala et al., 2001b). The condensation sink *CS'* is obtained by integrating over the aerosol size distribution:

$$\begin{aligned} CS' &= 2\pi D \int_0^\infty d_p \cdot \beta_M(d_p) \cdot n(d_p) dd_p \\ &= 2\pi D \sum_i \beta_{M_i} d_{p,i} N_i = 2\pi DCS \end{aligned} \tag{1}$$

where $n(d_p)$ is the particle size distribution function and N_i is the concentration of particles in the size section i. Here d_p is particle diameter, D is diffusion coefficient of condensable vapour, and for the transitional correction factor for the mass flux β_m we use the Fuchs-Sutugin expression (Fuchs and Sutugin, 1971).

The measured formation rate is smaller than the actual nucleation rate J* and determined by the competition between condensational growth (*GR* = growth rate from experimental observations) and scavenging (rate proportional to condensation sink *CS'*) (Kerminen and Kulmala, 2002):

$$J_m = J^* \exp\left\{0.23\left(\frac{1}{d_m} - \frac{1}{d^*}\right)\frac{CS}{GR}\right\} \tag{2}$$

Here *CS* is in units of m^{-2} and *GR* in units of nm/h. Setting the formation at 3 nm (J_3) and nucleation at 1 nm (J_1) gives

$$J_3 = J_1 \exp\left\{-0.153\frac{CS}{GR}\right\} \tag{3}$$

It is important to note that in deriving Eq. 2 (and thus also 3) a constant growth rate *GR* has been assumed. It has been seen, however, that the growth rate in the range 1–3 nm may be size dependent, caused presumably by organic vapour Kelvin effects (Kulmala et al., 2004b; Hirsikko et al., 2005). Since, in addition, Eq. (3) may be quite sensitive to *GR*, it should be considered as order-of-magntude estimate only.

It has been seen (e.g. Weber et al., 1996) that the formation rate of 3 nm particles can be expressed as a power-law dependence of the sulphuric acid concentration

$$J_3 \propto [H_2SO_4]^{n_3} \tag{4}$$

with a power-law exponent n_3. Correspondingly, we can assume that the formation rate of 1 nm particles has a similar dependence:

$$J_1 \propto [H_2SO_4]^{n_1} \tag{5}$$

By taking logarithms on each side, Eq. (3) can be rewritten as

$$\begin{aligned} \log(J_3) &= \log(J_1) - 0.153\frac{CS}{GR} \\ &= n_1 \log[H_2SO_4] - 0.153\frac{CS}{GR} \end{aligned} \tag{6}$$

Now, in addition to the nucleation rate terms J_1 and J_3, the sulphuric acid concentration $[H_2SO_4]$ can appear in Eq. (6) in the growth rate term *GR*. The formation rate dependence on $[H_2SO_4]$ is illustrated in Fig. 1. The curve representing J_1 is obviously a straight line, with the slope n_1 depending on the nucleation mechanism. If the effect of sulphuric acid on growth is negligible, i.e., the growth rate *GR* does not depend on $[H_2SO_4]$, then the term 0.153 *CS/GR* in Eq. (6) is constant (with respect to $[H_2SO_4]$). Hence the resulting apparent nucleation rate at 3 nm J_3 (Fig. 1) has the same slope as J_1, but a lower absolute value than J_1 by magnitude 0.153 *CS/GR*. If *GR* depends on $[H_2SO_4]$, the exact value for the slope is not straightforward to determine. In any case, it is clear that at otherwise the same conditions, increasing $[H_2SO_4]$ will increase *GR*, thus decreasing the magnitude of 0.153 *CS/GR*. This means that J_3 will approach J_1 at high values of $[H_2SO_4]$, as indicated qualitatively (dashed line) in Fig. 1. Thus the slope for J_3 should be steeper than the slope for J_1, (see also Laaksonen, 2000) i.e.,

$$n_1 \leq n_3 \tag{7}$$

One should notice that in our analysis J_1 and J_3 are compared for the "same" particles i.e. time shift is included. In principle coagulation between the growing particles will

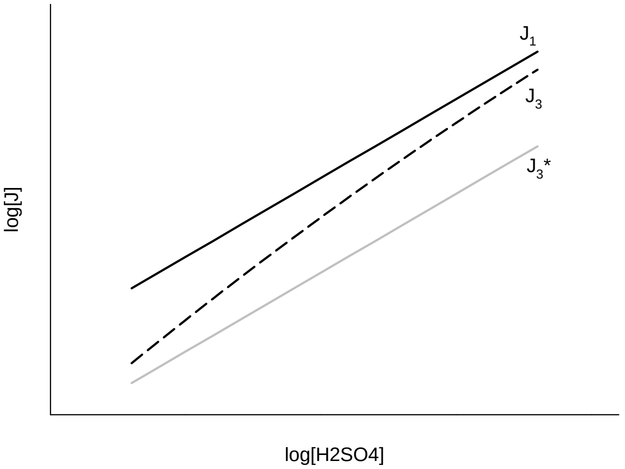

Fig. 1. Schematic dependence of apparent nucleation rate on sulphuric acid concentration. J_1 is the particle formation rate at 1 nm, J_3 the apparent particle formation rate at 3 nm and J_3* the apparent particle formation rate at 3 nm if sulphuric acid does not participate in growth.

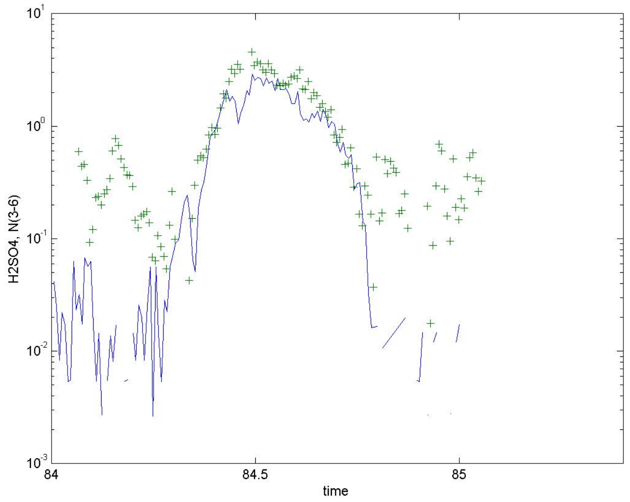

Fig. 2. Scaled small particle concentration (3–6 nm) (solid line) and scaled and time shifted (90 min ahead) sulphuric acid concentration (green +) measured in Hyytiälä in day 84 of the year, 2003.

complicate this analysis, however, in practise, intramodal coagulation is typically insignificant in atmospheric conditions.

The atmospheric measurements made by Weber et al. (1996) show that the slope for J_3 was between 1 and 2 in Idaho Hill. The recent measurement campaign (QUEST 2) (see Kulmala et al., 2004b) in Hyytiälä, Finland showed also that the slope is smaller than 2. In Fig. 2 the sulphuric acid concentration and the concentration of particles in size range 3–6 nm are plotted for one representative day of the campaign. The sulphuric acid concentration is measured by a chemical ionization mass spectrometer (see Fiedler et al., 2005) and particle size distribution by Differential Mobility Particle Sizer (DMPS) set up (see Aalto et al., 2001). The sulphuric acid concentration is scaled and also shifted 90 min ahead in time. This indicates the time needed for growth from nucleated size to 3 nm by condensation. The patterns of the curves are remarkably similar during daytime, indicating a linear relationship (i.e. a power-law exponent of unity) between these variables. Several event days during the campaign show such a clear linear dependence. Some other days shows better correlation with kinetic nucleation (power-law exponent of 2). We can, however, confidently state that in all cases the power-law exponent is between one and two.

According to the nucleation theorem the slope of nucleation rate vs. concentration of the nucleating vapour determines the number of molecules in the critical cluster (Kashchiev, 1982):

$$[\partial \ln(J)/\partial \ln(A_i)]_{T,Aj} = n_i + \Delta, \qquad (8)$$

where J denotes nucleation rate, A_i is the gas-phase activity (partial pressure divided by saturation vapor pressure) of species i, n_i is the number of molecules in the critical cluster, and Δ is a small term between 0 and 1 (Oxtoby and Kashchiev, 1994). It has been shown using both thermodynamic (Oxtoby and Kashchiev, 1994) and statistical mechanical (Viisanen et al., 1993; MacDowell, 2003) arguments that the nucleation theorem is a very general relation that extends down to the smallest cluster sizes and holds independently of any specific nucleation theories. Note that the derivatives should be taken at constant temperature and gas phase activities of other species participating in the nucleation process, and in atmospheric conditions, also at constant condensation sink.

Based on our observations the number n_1 must be pretty small, approaching unity. It is smaller than n_3, and n_3 is already two or smaller. This brings us to the question what is the mechanism responsible for n_1 being (at least near to) unity? Kinetic (barrierless) nucleation predicts that n_1 is 2, while thermodynamic binary nucleation theory for water + sulphuric acid predicts values bigger than 10, and ternary nucleation (with ammonia) values between 5 and 10 (see e.g. Bernd et al., 2005). How is it thus possible that n_3=1–2, as observed in the continental boundary layer, although n_3 should be bigger than n_1, and according to the above mentioned theories n_1 is more or equal than 2? One possible explanation is multicomponent nucleation with many more compounds participating than 3, and the other one is activation of existing clusters.

3 Activation of clusters

In the atmosphere ion clusters are practically always and everywhere present (see e.g. Laakso et al., 2004). Some studies predict also the existence of neutral clusters (e.g. Kulmala et al., 2000; Kulmala et al., 2005). Therefore, in principle,

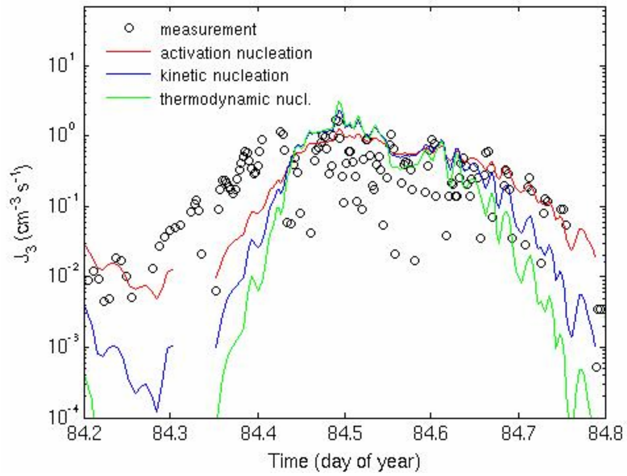

Fig. 3. Comparison of formation rates of 3 nm particles predicted by different theories and using observed number concentration. Hyytiälä DoY 84, 2003.

activation of neutral or ion clusters can explain the observed values of n_3.

The simplest way to describe the activation process is by using the concept of activation probability, such as in the theory of heterogeneous nucleation (see e.g. Lazaridis et al., 1992).

The time evolution of an activating cluster concentration can be estimated as

$$\frac{dN_{\text{clusters}}}{dt} = -kN_{\text{clusters}} \tag{9}$$

resulting in the well-known expression for activation probability P:

$$P = \frac{N_{\text{activated}}}{N_{\text{clusters}}} = 1 - \exp\left(-kt\right). \tag{10}$$

Here $N_{\text{activated}}$ is the number of activated clusters (actually aerosol particles), and N_{clusters} is the number concentration of clusters before activation, determined by sources (nucleation) and sinks (scavenging to existing particles). The cluster concentration can be estimated to be at pseudo steady state. k is a proportionality coefficient which is related to either a) heterogeneous nucleation, b) Köhler type activation or c) heterogeneous chemical reactions including polymerization.

Within the activation theory considered here, Eq. (9) translates into:

$$J_{act} = kN_{\text{clusters}}$$

where J_{act} denotes activation rate, and the formation rate at 3 nm resulting from the activation mechanism can be estimated similarly as in Eq. (2) as:

$$\begin{aligned} J_3 &= J_{\text{act}} \exp\left\{0.23\left(\frac{1}{3}-\frac{1}{d_{\text{act}}}\right)\frac{CS}{GR}\right\} \\ &= kN_{\text{clusters}} \exp\left\{0.23\left(\frac{1}{3}-\frac{1}{d_{\text{act}}}\right)\frac{CS}{GR}\right\} \end{aligned} \tag{11}$$

In which d_{act} is the size at which activation is occurring.

Now it is evident that if ion or neutral clusters containing 1 sulphuric acid molecule will activate the observed slope of unity is explained. As already mentioned ion clusters are ubiquitous. In addition, large amounts of neutral ammoniumbisulphate clusters have been recently predicted theoretically (Vehkamäki et al., 2004).

In the following we investigate how different theories used in nucleation will work as compared with observed number concentrations.

In the test we compare 3 different ways to estimate formation rates and compare it with the formation rate calculated from observed number concentration of 3–6 nm particles taking into account losses due to coagulation and condensation growth out of the size range.

$$J_{3,1} = C_1\,[\mathrm{H_2SO_4}]\exp\left\{0.23\left(\frac{1}{3}-1\right)\frac{CS}{GR}\right\} \tag{12a}$$

$$J_{3,2} = C_2\,[\mathrm{H_2SO_4}]^2\exp\left\{0.23\left(\frac{1}{3}-1\right)\frac{CS}{GR}\right\} \tag{12b}$$

$$J_{3,3} = C_3\,[\mathrm{H_2SO_4}]^3\exp\left\{0.23\left(\frac{1}{3}-1\right)\frac{CS}{GR}\right\} \tag{12c}$$

Equation (12a) describes activation theory, (12b) kinetic nucleation and (12c) is a conservative slope estimate for thermodynamic theories in general (slope value 3, which is smaller than typical value for thermodynamic nucleation).

The results are presented in Fig. 3. The best agreement seems to be with activation theory, i.e. Eq. (12a). The thermodynamic theory (Eq. 12c) gives clearly the worst predictions. This is particularly true during the morning and most of the daytime. From the fitted pre-factor C_i values one can also obtain estimates for the activation coefficient k (=C_1) and also for the kinetic pre factor (C_2), if kinetic nucleation is assumed. The typical growth time from 1 to 3 nm is 1000–10 000 s, and the GR for the day shown is 1.4 nm/h. The growth rate is pretty constant during the day but varies from day to day. The obtained values for the pre factors C_i are C_1~5e-7 (Activation). C_2~2e-13 and C_3~6e-20. However, observed constants vary from day to day. As a general result we can say that the present activation theory is consistent with nucleation events during which the 3 nm particle appearance rate depands linearly on sulphuric acid concentration. However, as seen from figure, all theories underestimate measured formation rates before noon. This means that e.g. the activation coefficient should be a factor of 10–100 higher than given at that time. Taking into account observed overcharging of small clusters during that morning (see Laakso et al., 2004), this indicates that activation coefficient for ion activation is higher and the ions are activated first (before noon) and activation of neutral clusters occurs somewhat later.

The day to day variation of activation constant can be explained by variation of concentrations of other vapours. It can be estimated that quite often organic vapours are needed for activation. The organic vapour can participate in the activation processes via a) heterogeneous reactions (Claeys et al., 2004), b) polymerization (Kalberer et al., 2004), c) heterogeneous nucleation or Nano-Köhler (see Kulmala et al., 2004c). Actually, the observed k value for the activation mechanism can be explained by product of concentration of collided molecules (around 1e7–1e8 cm^{-3}) and typical chemical reaction rate in gas phase.

As mentioned above, in the activation process, there are other vapours present as sulphuric but what is their contribution to the observed aerosol formation rate J_3? In the case of multicomponent homogeneous nucleation, the nucleation theorem will tell us, what would be their contribution. In the case of heterogeneous nucleation the contribution will depend on contact angle and the ratio of sizes of seed particle and critical cluster (Määttänen et al., 2005; Kulmala et al., 2001; Vehkamäki et al., 2005). The number of molecules in the critical cluster are often ten times smaller than in homogeneous case.

4 Conclusions

Current estimates of the magnitude of regional and global secondary aerosol formation rely almost entirely on modeling and are subject to large uncertainties. There are uncertainties in identifying both the detailed nucleation mechanisms as well as the nucleation rates. In this paper we present a method with which we can obtain hints about the formation mechanisms indirectly: by comparing sulphuric acid concentrations with particle concentrations between 3 nm and 6 nm, clear similarities are observed in their time evolution. The particle concentration seems to have a power-law dependence on the sulphuric acid concentration, with an exponent value between 1 and 2. A theoretical investigation of the connection between different exponent values and nucleation mechanisms shows that particle nucleation proceeds likely by either a kinetic mechanism or by activation mechanism.

The activation mechanism is based on the concept of activation probability. This is commonly used in studies of heterogeneous nucleation (see e.g. Kulmala et al., 2001; Wagner et al., 2003). In practice the activation probability can depend on, in addition to heterogeneous nucleation, also on heterogeneous chemical reactions including polymerization and activation of mutually soluble compounds, like in nano-Köhler theory. The activation constant is in the order of 1e-6–1e-7 1/s. In the proposed activation mechanism neutral or ion clusters containing one sulphuric acid molecule are activated for further growth. This can directly explain the observed relationship between sulphuric acid concentration and fresh particle formation with a slope of unity.

Acknowledgements. Discussions and help by V.-M. Kerminen and S.-L. Sihto and the financial support from the Academy of Finland are acknowledged.

Edited by: K. Hämeri

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