

Parameterization of new particle formation starting from OH + SO₂

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Simultaneous measurements of newly formed ultra-fine particles and H₂SO₄ in the lower troposphere reveal that new particle formation is strongly connected to the occurrence of H₂SO₄ with concentrations of about 10⁵ - 10⁷ molecule cm⁻³ and the production rate of new particles can be described by a power law equation for H₂SO₄ with an exponent in the range of 1 - 2 (Weber et al., 1996, Kulmala et al., 2006).

From our laboratory, using the reaction of OH radicals with SO₂ for “H₂SO₄” formation (Berndt et al., 2005), experimental evidence for the formation of new particles was found for “H₂SO₄” concentrations of ~10⁷ molecule cm⁻³. Here, “H₂SO₄” stands for all products arising from the reaction of OH radicals with SO₂. The analysis of integral number measurements by means of commercially available UCPCs revealed that measured slopes of log(N) vs. log([“H₂SO₄”]) were affected by the decreasing size-dependent counting efficiency of the UCPCs used for dp < 3 nm leading to an overestimation of the slopes.

The aim of this study is to find out the optimal experimental conditions for the detection of the majority of nucleated particles with appropriate methods. Such data represent the basis for a reliable description of the overall process of nucleation in term of a power equation.

The nucleation experiments have been carried out in the atmospheric pressure flow-tube IfT-LFT (i.d. 8 cm; length 505 cm) at 293 ± 0.5 K. For integral particle measurements a butanol-based UCPC (TSI 3025), a H₂O-based UCPC (TSI 3786) as well as a pulse height condensation particle counter (PH-CPC) have been used. In order to measure particle size distributions a differential mobility particle sizer (DMPS) consisting of a Vienna-type DMA and a butanol-based UCPC (TSI 3025) came into operation.

In Figure 1 experimental data of measured particle numbers vs. [“H₂SO₄”] are depicted measured simultaneously by means of three different UCPCs (TSI 3025, TSI 3786, PH-CPC) as well as by

DMPS (dp ≥ 3 nm). The IfT-LFT was operated with a residence time of 290 sec and r.h. = 22%.

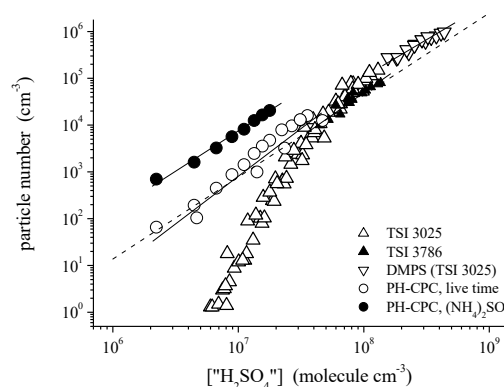


Figure 1. Measured particle numbers as a function of “H₂SO₄” concentration at r.h. = 22 % for a residence time of 290 sec.

The slopes log(N) vs. log([“H₂SO₄”]) span a range of 1.58 - 2.03 (DMPS: 1.58 ± 0.05; TSI 3786: 1.91 ± 0.11; PH-CPC, live time: 2.03 ± 0.01; PH-CPC, (NH₄)₂SO₄: 1.70 ± 0.06).

In further experiments, for several fixed “H₂SO₄” concentrations new particle formation was investigated as a function of relative humidity (or H₂O vapour concentration). Putting all measurements together, the overall best fit according to equation

$$N = k ([\text{“H}_2\text{SO}_4\text{”}] / \text{molecule cm}^{-3})^\alpha ([\text{H}_2\text{O}] / \text{molecule cm}^{-3})^\beta$$

yielded $\alpha = 1.76 \pm 0.02$ and $\beta = 1.54 \pm 0.04$.

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