Supplementary Material

Estimation of Wall Loss of Sulfuric Acid in the Fast Flow Nucleation Reactor:

We have calculated wall loss factors (WLF) of H₂SO₄ by assuming that wall loss is diffusion-limited based on Hanson and Eisele (2002). WLF is defined as:

\[ \text{WLF} = \frac{[\text{H}_2\text{SO}_4]_0}{[\text{H}_2\text{SO}_4]_t} \quad (\text{Eq. s1}) \]

where \([\text{H}_2\text{SO}_4]_0\) is the initial concentration, \([\text{H}_2\text{SO}_4]_t\) is the H₂SO₄ concentration after the nucleation time of \(t\). H₂SO₄ wall loss can be expressed with the first order rate constant, \(k\), in a fast flow reactor:

\[ [\text{H}_2\text{SO}_4]_t = [\text{H}_2\text{SO}_4]_0 e^{-kt} \quad (\text{Eq. s2}) \]

\(k\) is diffusion-limited (Hanson and Eisele, 2000):

\[ k = \frac{3.65D}{r^2} \quad (\text{Eq. s3}) \]

where \(D\) is the diffusion coefficient, and \(r\) is the radius of the flow reactor. \(D = 0.094 \text{ cm}^2\text{s}^{-1}\) for a RH of 20% and at the atmospheric pressure [Hanson and Eisele, 2000]. Under the typical experimental conditions \((r = 2.54 \text{ cm})\), the calculated \(k\) is thus 0.053 s⁻¹. In this method, condensation loss is assumed to be negligible. The estimated WLFs are shown in Table 1 in the main text.

Viisanen et al. (1997) have reported WLF of H₂SO₄ of 1.7 (that is, 40% loss on the wall) for nucleation time of 3.3 s from their gas-liquid nucleation of H₂SO₄-H₂O experiments where a laminar flow diffusion chamber \((r = 1.2 \text{ cm})\) was used as the nucleation reactor. Ball et al. (1999) used a fast flow reactor in their H₂SO₄-H₂O BHN experiments and estimated a factor of 2 loss of H₂SO₄ in the “nucleation zone” (corresponding nucleation time was 4 s, although the
residence time in the entire flow reactor was ~ 12 s) (r = 2.45 cm). By further including other
additional factors, such as losses on several joints inside the nucleation reactor, Ball et al. (1999)
have reported an overall WLF of 22. The WLF estimations from these two cited studies are
consistent with the values derived by assuming that wall loss is diffusion-limited, regardless of
their differences in the nucleation reactor’s dimension and nucleation time. In comparison, our
WLF is 2.6 calculated for the lowest nucleation time of 20 s used in the present study (r = 2.45
cm).

References:

Ball, S. M., D. R. Hanson, F. L. Eisele, and P. H. McMurry, Laboratory studies of particle
nucleation: Initial results for H2SO4, H2O, and NH3 vapors, J. Geophys. Res., 104, 23709-
23718, 1999.

Hanson, D. R., and F. Eisele, Diffusion of H2SO4 in humidified nitrogen: Hydrated H2SO4, J.

Seinfeld, J. H., and S. N. Pandis, Atmospheric chemistry and physics, from air pollution to

Viisanen, Y., M. Kulmala, and A. Laaksonen, Experiments on gas-liquid nucleation of sulfuric
Figure s1. The Kent State University experimental setup for H$_2$SO$_4$-H$_2$O binary homogeneous nucleation kinetics. This setup consists of an OH generator, a fast-flow nucleation reactor, an atmospheric pressure chemical ionization mass spectrometer (CIMS), a nanoparticle differential mobility analyzer (nano-DMA) and a water condensation particle counter (WCPC).
Time in the Reactor

Concentration of molecules

$[\text{OH}]_0 = 1.50 \times 10^9 \text{ cm}^{-3}$
$[\text{H}_2\text{SO}_4]_0 = 1.29 \times 10^9 \text{ cm}^{-3}$

$[\text{H}_2\text{SO}_4]_w = \frac{1}{2} [\text{H}_2\text{SO}_4]_0$
$[\text{H}_2\text{SO}_4]_w = 4.63 \times 10^8 \text{ cm}^{-3}$
$[\text{H}_2\text{SO}_4]_{\text{CIMS}} = 8.22 \times 10^8 \text{ cm}^{-3}$

$[\text{H}_2\text{SO}_4]_p = 2.48 \times 10^3 \text{ cm}^{-3}$
Figure s2. The simulated aerosol precursor concentrations as a function of reaction time for the nucleation time of 22s (a), 38 s (b), and 54 s (c). WLFs are calculated by assuming that wall loss is diffusion-limited. $[\text{H}_2\text{SO}_4]_p$, $[\text{H}_2\text{SO}_4]_{\text{CIMS}}$, $[\text{H}_2\text{SO}_4]_w$, and $[\text{H}_2\text{SO}_4]_0$ indicate the $[\text{H}_2\text{SO}_4]$ in the particle-phase, that measured by CIMS, that taken by the wall, and the initial concentrations in the nucleation reactor, respectively. $[\text{H}_2\text{SO}_4]_p$ is calculated based on the volume concentrations from CPC or SMPS measurements, by assuming that the newly formed particles are spherical and are composed of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ (with a particle density of 1.4 g cm$^{-3}$) only. SMPS provides directly volume concentrations. For the CPC data, we assume that particles are monodisperse particles with the median diameter of 4 nm. $[\text{H}_2\text{SO}_4]_0 = \text{WLF} \times ([\text{H}_2\text{SO}_4]_{\text{CIMS}} + [\text{H}_2\text{SO}_4]_p)$. $[\text{H}_2\text{SO}_4]_w = (\text{WLF} - 1) \times ([\text{H}_2\text{SO}_4]_{\text{CIMS}} + [\text{H}_2\text{SO}_4]_p)$. For most of the experimental conditions, $[\text{H}_2\text{SO}_4]_{\text{CIMS}} \gg [\text{H}_2\text{SO}_4]_p$. The gas phase reaction schemes and their rate constants used in this simulation are: (i) $\text{H}_2\text{O} + \text{UV (λ = 149.5 nm)} \rightarrow \text{OH} + \text{H} \ (J_{\text{H}_2\text{O}} = 9.7 \times 10^{-6} \ \text{s}^{-1}$ under the typical
experimental conditions) [L.-H. Young et al., Laboratory studies of sulphuric acid and
water binary homogeneous nucleation: Preliminary results, a manuscript to be submitted
to *Atmos. Chem. Phys.*] from 0 – 0.3 s, (ii) OH + CO + O₂ → CO₂ + HO₂ (k = 2.4 × 10⁻¹³
\(\text{cm}^{-3} \text{s}^{-1}\)) [Seinfeld and Pandis, 1997] from 0.3 – 1.3 s, and (iii) SO₂ + OH → HSO₃ (k =
1.5 × 10⁻¹² \(\text{cm}^{-3} \text{s}^{-1}\)) [Seinfeld and Pandis, 1997]. The OH photolysis time is 0.3 s. [OH]
was changed by changing the water vapor concentrations and under the typical
experimental condition, the generated [OH] at the 10⁸ - 10⁹ \(\text{cm}^{-3}\) range for RH from 10 -
50 %. Different [OH] will result in different [H₂SO₄]. 86% of the OH radicals generated
from water UV photolysis remain after the CO + OH (+ O₂) → CO₂ + HO₂ reaction for
100 ppbv [CO] impurities (originating from the nitrogen gases blown from liquid
nitrogen) and a reaction time of 1 s (representing the distance of 9 cm from the photolysis
region to the point where SO₂ and O₂ are introduced; i.d. = 5.08 cm). Thus, the produced
[OH] = \([\text{H}_2\text{SO}_4]_0/0.86\). Total flow is 2.5 l min⁻¹ at the typical condition. Nitrogen gages
introduced to produce water vapor at the uppermost stream are the main flow in the
system and hence the further dilution by SO₂ and O₂ gases is negligible. The reaction
time of SO₂ + OH → HSO₃ is very short (< 1 ms at [SO₂] (ppmv) \(\gg\) 1000 × [OH]). As
soon as \(\text{H}_2\text{SO}_4\) is formed, nucleation, condensation and wall loss of \(\text{H}_2\text{SO}_4\) take place in
the nucleation reactor. Because of wall loss, the gas phase \([\text{H}_2\text{SO}_4] = [\text{H}_2\text{SO}_4]_0 e^{-kt}\);
typically \(k = 0.053 \text{s}^{-1}\) (as mentioned in the supplement text here). Note that the times
and concentrations shown here represent the true values, but they are shown not at the
actual scales.
Figure s3. The CIMS-measured [H$_2$SO$_4$] as a function of the particle number concentration for the same dataset shown in Figure 2a-2c in the main (for experimental conditions, see Table 1). At larger particle concentrations (50,000 cm$^{-3}$), the CIMS-measured [H$_2$SO$_4$] start to level off and eventually decrease at very high concentrations (200,000 cm$^{-3}$), even though the initial [SO$_2$] and the CIMS-measured [H$_2$SO$_4$] are increasing, because of the H$_2$SO$_4$ condensation losses for high particle concentrations.