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Temperature-dependent diffusion coefficient of H_2SO_4 in air: laboratory measurements using laminar flow technique

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Abstract

We report measurements of the diffusion coefficient of sulfuric acid in humidified air at a range of relative humidities (from ~4 to 70 %), temperatures (278, 288 and 298 K) and initial H_2SO_4 concentration (from 1×10^6 to 1×10^8 molec. cm^{-3}). The diffusion coefficients were estimated from the sulfuric acid wall loss rate coefficients under laminar flow conditions. The flow conditions were verified with additional fluid dynamics model CFD-FLUENT simulations which also reproduced the loss rate coefficients very well at all three temperatures with the maximum difference of 7 % between the measured and simulated values. The concentration of H_2SO_4 was measured continuously with chemical ionization mass spectrometer (CIMS) at seven different positions along the flow tube. The wall losses of H_2SO_4 were determined from the slopes of fits to measured H_2SO_4 concentrations as a function of the position along the flow tube. The observed wall loss rate coefficients, and hence the diffusion coefficients, were independent of different initial H_2SO_4 concentrations and different total flow rates. However, the determined diffusion coefficients decreased with increasing relative humidity, as also seen in previous experiments, and had a rather strong power dependence of the diffusion coefficient with respect to temperature, around $\propto T^{5.4}$, which is in disagreement with the expected temperature dependency of $\sim T^{1.75}$ observed for other gases and not tested before for sulfuric acid. The effect of relative humidity on the diffusion coefficient is likely due to stronger hydration of H_2SO_4 molecules and likely also due to the presence of trace impurities such as amines, possibly brought to the system by humidification. Clustering kinetics simulations using quantum chemical data suggest that also the strong temperature dependence of the observed diffusion coefficient might be explained by increased diffusion volume of H_2SO_4 molecules due to stronger clustering with base-impurities like amines.

1. Introduction

Sulfate aerosols play a dominant role in atmospheric chemistry and have undoubtedly influence on humans' health and Earth's climate. Gas phase sulfuric acid is formed via oxidation reaction of SO_2 with OH radicals. The loss of gaseous H_2SO_4 in the atmosphere is caused by new particle formation events, acid-base reactions and cluster formation, and condensation on pre-existing atmospheric particles. The growth of a particle is driven by condensation of surrounding vapour on its surface, and the diffusion coefficient (D) of H_2SO_4 is often used in mass transport calculations in aerosol chemistry and physics. Condensation and evaporation rates are key parameters in aerosol dynamics models, and the accuracy of these rates is highly dependent on

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the values used for the binary diffusion coefficients (Seinfeld and Pandis, 1998). Under certain circumstances, the gas phase diffusion can even limit the overall rates of condensation and reactions of trace gases with aerosol particles via influencing the uptake of gas molecules onto the surface (Tang et al., 2014). The factor that determines if a H_2SO_4 molecule will attach to pre-existing aerosol or stay in the gas phase, possibly contributing to subsequent new particle formation, is the mass accommodation coefficient (Pöschl et al., 1998). Together with information on the mass accommodation coefficient, detailed knowledge on the diffusion coefficient is necessary for accurately simulating atmospheric condensation processes.

In this paper we report laboratory measurements of the diffusion coefficient of sulfuric acid in air. The diffusion coefficient of H_2SO_4 was estimated from the first order rate coefficients of the wall losses of H_2SO_4 in a flow tube. The measurements were conducted at atmospheric pressure under different experimental conditions in order to assess the effect of temperature, relative humidity, residence time and initial H_2SO_4 concentration on the diffusion coefficient of H_2SO_4.

All previous measurements of the sulfuric acid diffusion coefficient have been carried out using nitrogen as the carrier gas and a laminar flow technique. Pöschl et al. (1998) studied the gas-phase diffusion of H_2SO_4 at T=303 K, Lovejoy and Hanson (1996) performed experiments at T=295 K, and Hanson and Eisele (2000) at T=298 K. To our best knowledge, we here present the first study that investigates systematically the temperature dependency of the diffusion coefficient of H_2SO_4. In a previous study (Hanson and Eisele, 2000) the RH dependency of H_2SO_4 diffusion was investigated, but results reporting the temperature dependency have not been published before.

The Chapman-Enskog theory on gas kinetics predicts the binary diffusion coefficient to depend on the temperature as $D \propto T^{1.5}$ when approximating the gas molecules as hard spheres. Fuller et al. (1966) used a semi-empirical method based on the best nonlinear least square fit for a compilation of 340 experimental diffusion coefficients, and obtained a temperature dependence of $T^{1.75}$. The Fuller et al. method is known to yield the smallest average error, hence it is still recommended for use (Reid et al., 1987). According to a compilation work of Marrero and Mason (1972), the temperature dependence of diffusion coefficients in binary gas mixtures in most cases varies between $T^{1.5}$and T^2. However, gaseous sulfuric acid vapour can undergo strong clustering due to presence of base impurities, as noted in several previous experiments (e.g. Petäjä et al 2011; Almeida et al., 2013; Neitola et al. 2015, Rondo et al. 2016). Such base impurities are unavoidably present also in our experiment, and most probably they originate

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from the humidification of the carrier gas (e.g. Benson et al., 2011; Kirkby et al., 2011; Neitola et al. 2015). Cluster kinetic simulations have suggested that the diffusion coefficient of sulfuric acid is likely sensitive to such clustering (Olenius et al., 2014), which on the other hand is sensitive to temperature. Here, we use several approaches to verify the experimental method, and examine our results against the predictions of the semi-empirical formula as well as data from the previous experiments. In addition, we assess the effect of molecular cluster formation by cluster kinetics simulations with quantum chemical input data.

2. Methods

The experimental setup used in this study was described in detail in our previous work (Neitola et al., 2014; Skrabalova et al., 2014) and therefore only a brief description is given here. The whole experimental apparatus consists of four main parts: a saturator, a mixing unit, a flow tube and the sulfuric acid detection system – Chemical Ionization Mass Spectrometer (CIMS) (Eisele and Tanner, 1999), presented in Figure 1. The H_2SO_4 wall loss measurements were carried out in a laminar flow tube at three temperatures of 278.20(±0.2), 288.79(±0.2), and 298.2(±0.2) K using purified, particle free and dry air as a carrier gas. The flow tube is a vertically mounted cylindrical tube made of stainless steel with an inner diameter (I.D.) of 6 cm and a total length of 200 cm. The whole flow tube was insulated and kept at a constant temperature with two liquid circulating baths (Lauda RK-20). The flow tube consists of two 1 meter long parts; one of them is equipped with 4 holes in the distance of 20 cm from each other, see Figure 1. Sulfuric acid vapour was produced by passing a stream of carrier gas through a saturator filled with 95-97 % wt. sulfuric acid (J.T. Baker analysed). As a saturator we used a horizontal iron cylinder with Teflon insert (I.D. 5 cm) and it was thermally controlled using a liquid circulating bath (LAUDA RC-6). The temperature inside the saturator was measured with a PT100 thermocouple (± 0.05 K). The carrier gas saturated with H_2SO_4 was then introduced with a flow rate from 0.1 to 1 l min^{-1} into the mixing unit made of Teflon and turbulently mixed with a stream of humidified particle free air. The gas mixture was then introduced into the flow tube. The flow rate of the mixing air varied in most of the experiments from about 7 to 10 l min^{-1}. The mixing air was humidified with one pair of Nafion humidifiers (Perma Pure MH-110-12) connected in parallel, where the flow of the mixing air was split into half for longer residence time and better humidification in both humidifiers. Ultrapure water (Millipore, TOC less than 10 ppb, resistivity 18.2 MΩ.cm @25°C) circulating in both humidifiers was temperature controlled with liquid circulating bath (Lauda RC-6 CS). The mixing unit was kept at room temperature and it was not

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insulated. The mixing unit had following dimensions: O.D. = 10 cm, I.D. = 7 cm and height = 6 cm. Both lines of the carrier gas (saturator and mixing air) were controlled by a mass flow controller to within ±3 % (MKS type 250). The relative humidity was measured at the centre and far end of the flow tube with two humidity and temperature probes (Vaisala HMP37E and humidity data processor Vaisala HMI38) within accuracy of ± 3 %.

The sulfuric acid diffusion coefficients were estimated as a function of relative humidity from the H_2SO_4 loss measured by CIMS along the flow tube. The detailed information regarding the operational principles and calibration of CIMS is given in Eisele and Tanner, (1993); Mauldin et al., (1998) and Petäjä et al., (2009) and therefore will not be given here again. The charging and detection efficiency of CIMS in the presence of trace concentrations of base impurities is discussed thoroughly theoretically (e.g. Kupiainen-Määttä et al., 2013; Ortega et al., 2014) and also in recent experimental reports (e.g. Neitola et al., 2015; Rondo et al., 2016). Possible attachment of base and/or water molecules to single H_2SO_4 molecules is not expected to have a notable effect on their detection efficiency. However, both free H_2SO_4 molecules and those bound to base and/or water molecules are detected as single H_2SO_4 molecules by CIMS, since the ligands are quickly lost upon the chemical ionization (e.g. Ortega et al., 2014). In this study the actual H_2SO_4 concentrations are not of particular interest, we focus here only on relative loss of H_2SO_4 along the flow tube. The concentration of sulfuric acid in gas phase was measured as 97 m/z Da using CIMS along the flow tube (see Fig. 1) at the beginning (0 cm), in the middle (100 cm) and at the lower part in distances of 120, 140, 160, and 180 cm from the beginning and at the outlet (200 cm) of the flow tube in a wide range of relative humidities from 4 to 70 %. The CIMS sampling flow rate was set to 7 l min^{-1}. In order to measure the H_2SO_4 concentration along the whole flow tube, an additional CIMS inlet sampling tube was used - a stainless steel tube with I.D. 10 mm and whole length of 122 cm (100 cm straight + 22 cm elbow-pipe). The experimental measurement proceeded in the following way. First, all the experimental conditions (temperature of saturator and flow tube, flow rates, relative humidity) were adjusted. When the steady state was reached, the CIMS' inlet was connected to the lowest hole at 200 cm and concentration of sulfuric acid was recorded for at least 20 min. Afterwards the CIMS' inlet was moved up to the hole at 180 cm, and the same procedure was repeated until the last hole at the top of the tube was reached. To confirm the reproducibility of the experimental data the H_2SO_4 concentration at any arbitrary distance along the flow tube was measured again. Moreover, the reproducibility was checked by exchanging the flow tube parts, so that the part with 4 holes was

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151 moved up, and H_2SO_4 losses were measured in the distances 0, 20, 40, 60, 80, 100 and 200 cm,
152 respectively.

153 2.1 The CFD model

154 To verify the assumption of laminar flow inside the tube, we applied the computational fluid
155 dynamics model CFD-FLUENT (version 6.2) which simulates flow based on the Euler equations
156 for mass and momentum conservation. These equations and the general operating principles of
157 FLUENT are described in detail in Herrmann et al. (2006, 2009 and 2010). It has to be noted that
158 unlike the earlier studies, this work did not include the Fine Particle Model (FPM). Particle
159 production was thus not taken into account, and only sulfuric acid and water vapours are
160 considered in the CFD-FLUENT simulations.

161 The simulations only considered the flow tube part of the experimental setup described in section
162 2. Methods; the flow tube can be set up as an axisymmetric 2D problem. For the calculations
163 presented here, we chose a resolution of 50×1000 cells. The same geometry has been used in
164 Herrmann et al. (2010). Boundary conditions (volumetric flow, wall temperatures, relative
165 humidity, and initial sulfuric acid concentration) were set to match the experimental conditions.
166 The wall was assumed to be an infinite sink for sulfuric acid, which means that the H_2SO_4
167 concentration at the walls was set to 0 in the simulations. Properties of sulfuric acid were
168 identical to the ones described in our earlier work. Differing from Herrmann et al. (2010), there
169 is no temperature gradient or buoyancy phenomena disturbing parabolic radial flow profile. To
170 verify the proper operation of the setup we applied the diffusion coefficient derived
171 experimentally in this work to FLUENT simulations. The simulations yielded a profile of
172 sulfuric acid concentration inside the flow tube which we compared back to the experimental
173 results.

174 2.2 Experimental determination of the diffusion coefficient

175 The wall loss of H_2SO_4 in the flow tube was assumed to be a diffusion controlled first-order rate
176 process, which can be described by a simple equation:

177 $$[H_2SO_4]_t = [H_2SO_4]_0 \, e^{-kt}, \quad (1)$$

178 where $[H_2SO_4]_0$ is the initial concentration of H_2SO_4, $[H_2SO_4]_t$ is the concentration after time t
179 and k (s^{-1}) is the rate constant, which is given by the equation:

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$$k = 3.65 \frac{D}{r^2}, \quad (2)$$

where r is the radius of the flow tube and D is the diffusion coefficient of H_2SO_4. Equation 2 is valid for diffusion in a cylindrical tube under laminar flow conditions and when the axial diffusion of the species investigated is negligible (Brown, 1978). The slopes obtained from linear fits to the experimental data ln([H_2SO_4]) as a function of the distance in the flow tube stand for the loss rate coefficient, k_{obs} (cm^{-1}) assuming that the first order loss to the flow tube wall is the only sink for the gas phase H_2SO_4. Multiplying the loss rate coefficient k_{obs} with mean flow velocity in the flow tube (cm s^{-1}) yields the experimental first-order wall loss rate coefficient k_w (s^{-1}), from which the diffusion coefficients of H_2SO_4 were determined using Eq. 2. Hanson and Eisele (2000) reported that the wall of the flow tube can act as a source of H_2SO_4 vapour after exposure in long lasting experiments and under very low relative humidity (RH ≤ ~0.5%). The accuracy of our RH measurements is ± 3 % RH, so to avoid any influence of H_2SO_4 evaporation from the flow tube wall we only used data measured at RH ≥ 4 % in the final analysis. Furthermore, we performed CFD-FLUENT simulations at RH=5 % and T=298 K, with increased H_2SO_4 concentration on the flow tube wall (0-100 % of [H_2SO_4]$_0$), shown in Fig. 2. The comparison suggests that in our measurements the concentration on the flow tube wall is below 6 % of the [H_2SO_4]$_0$ under all conditions. When the H_2SO_4 concentration on the wall is ≤ 6 % of [H_2SO_4]$_0$, the resulting difference in the obtained diffusion coefficient is within 10 % when compared to diffusion coefficient obtained with infinite sink boundary condition on the wall, as indicated by the shaded box in bottom left corner in Fig 2B. Any higher H_2SO_4 concentration at the wall than 6 % of [H_2SO_4]$_0$ would lead to a larger than 10 % decrease in the obtained diffusion coefficient.

2.3 Quantum chemical data and cluster kinetics modeling

To assess the effects of possible base impurities on the measurement results, we performed clustering kinetics simulations using quantum chemical input data for the stabilities of H_2SO_4–base clusters as described by Olenius et al. (2014). Since recent theoretical studies (e.g. Ortega et al., 2012; Kupiainen-Määttä et al., 2013; Loukonen et al. 2014) suggest and experiments (e.g. Zollner et al. 2012; Almeida et al. 2013; Kürten et al., 2014; Neitola et al., 2014, Rondo et al. 2016) confirm that amines are more effective in stabilizing sulfuric acid clusters than ammonia, we focus only on the clustering of sulfuric acid with dimethylamine (DMA) and trimethylamine (TMA) and their hydrates (see also Section 3.2 Effect of Base Contaminants in Olenius et al.,

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2014).The cluster kinetics approach does not consider the 2D flow profile, but only the central stream line of the flow, from which clusters and molecules are lost by diffusion. This is considered a reasonable assumption for a laminar flow, as also indicated by the CFD-FLUENT modeling results (see the Results section).

Detailed information on the simulations, as well as extensive discussion on the effects of clustering on the apparent diffusion coefficient can be found in the study by Olenius et al. (2014). Theoretical diffusion coefficients for sulfuric acid and representative base contaminant molecules and small acid–base clusters and their hydrates were calculated according to the kinetic gas theory. The effective diffusion coefficient corresponding to the experimental approach was determined by simulating the time evolution of the molecular cluster concentrations using cluster evaporation rates based on quantum chemical calculations at the B3LYP/CBSB7//RICC2/aug-cc-pV(T+d)Z level of theory, as described by Olenius et al. (2014). The simulations were run by setting initial concentrations for H_2SO_4 and base monomers, and integrating the time development of the cluster concentrations for the experimental residence times. The initial acid concentration was set to be the average H_2SO_4 monomer concentration $[H_2SO_4]= 5\times10^6$ cm^{-3} measured with CIMS at the beginning of the flow tube (see Fig. 1, hole 1) for all experimental conditions. For the initial base concentration we adopted a similar approach as described in Olenius et al. (2014): The initial base concentration was considered to be a) constant during the experiment, or b) RH dependent, i.e. base molecules enter the system with the water vapour; such a scenario seems to be reasonable since it was observed in several experimental set-ups (e.g. Benson et al., 2011; Brus et al., 2011; Kirkby et al., 2011). In the second case we set the initial base concentration $[base]_{init}$ to be linearly proportional to RH as

$$[base]_{init}\,(ppt) = [base]_{dry}\,(ppt) + 0.1\times RH\,(\%), \quad (3)$$

where the linear relationship was based on a fit to DMA and TMA concentrations measured in the same experimental setup, but different experiments at various RH and H_2SO_4 concentrations (Neitola et al., 2014 and 2015). The dry values $[base]_{dry}$ were taken from Brus et al., (2016). The resulting initial base concentrations $[base]_{init}$ for DMA and TMA were 4 and 2 ppt, respectively, at dry conditions (RH=0 %), and 10 and 8 ppt at RH=60 %. The simulations were performed for the three temperatures of 278, 288 and 298 K at atmospheric pressure (1 atm). The temperature dependency of the viscosity of the carrier gas, needed to calculate the diffusion coefficients of different species in the simulations (see Eq. (6) in Olenius et al., 2014), was taken to be

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$$\eta_{N_2} = \eta_{N_2,0}\left(\frac{T_0+C}{T+C}\right)\left(\frac{T}{T_0}\right)^{3/2}, \quad (4)$$

where $\eta_{N_2,0}$ = 17.81×10^{-6} Pa s, T_0 = 300.55 K, and C =111 K (Crane Co., 1982).

3. Results and discussion

Figure 3 shows the diffusion coefficients of H_2SO_4, determined from the loss rate coefficients k_w (s^{-1}) using Eq. 2 as a function of RH at the three temperatures of 278, 288 and 298 K. The measured points are accompanied with the fit and H_2SO_4 - N_2 data at 298 K reported by Hanson and Eisele (2000). As can be seen, the diffusion coefficient values decreased as the RH was increased and the diffusion coefficient dependency on RH flattens in the range of RH 20-70 %. These results show lower wall losses and slower diffusion to the wall due to strong hydration of H_2SO_4 molecules (Jaecker-Voirol and Mirabel, 1988) and possibly H_2SO_4 clustering with base impurities.

There are three previously reported experimental values of the H_2SO_4 diffusion coefficient in nitrogen. Pöschl et al. (1998) reported a value of 0.088 cm^2 s^{-1} at T=303 K and RH ≤ 3%, Lovejoy and Hanson (1996) reported a value of 0.11 cm^2 s^{-1} at T=295 K and RH ≤ 1%, and the study of Hanson and Eisele (2000) yielded a value of 0.094 cm^2 s^{-1} at T=298 K and RH ≤ 1%. The value of the diffusion coefficient of H_2SO_4 in air at T=298 K and RH=4 % determined in this study is 0.08 cm^2s^{-1}, which is in reasonable agreement with previously reported values, although the comparison is complicated because of slightly different experimental conditions and different carrier gases.

In Fig. 4 the H_2SO_4 losses simulated with the CFD-FLUENT model described in section 2.1 are compared with experimental values, which were measured in a separate set of experiments conducted at T=278, 288 and 298 K. The linear fit to the experimental data represents the loss rate coefficients (k_{obs}, cm^{-1}). As can be seen from Fig. 4, the model describes the behaviour of H_2SO_4 in the flow tube very well and confirms the validity of laminar flow approximation for all three temperatures. The maximum difference between the experimental and simulated values of the loss rate coefficient (k_{obs}) was found 7 %, see Fig. 4D for details.

Semi-empirical predictions for binary diffusion coefficients can be calculated from the Fuller et al. equation which is based on fits to experimental data of various gases as described by Fuller et al. (1966) and Reid at al. (1987):

$$D_{AB} = \frac{0.00143T^{1.75}}{P\sqrt{M_{AB}}\times\left[\sqrt[3]{(\Sigma_v)_A}+\sqrt[3]{(\Sigma_v)_B}\right]^2}, \quad (4)$$

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where D_{AB} is the binary diffusion coefficient of species A and B ($cm^2\ s^{-1}$), T is the temperature (K), P is the pressure (bar), M_{AB} is $2[(1/M_A) + (1/M_B)]^{-1}$ (g mol^{-1}), where M_A and M_B are the molecular weights of species A and B (g mol^{-1}), and $\sum_v$ is calculated for each component by summing its atomic diffusion volumes (Reid at al., 1987). The functional form of Eq. (4) is based on the kinetic gas theory (the Chapman-Enskog theory), and the temperature dependence is obtained from a fit to a large set of experimental diffusion coefficients. A purely theoretical approach based on the kinetic gas theory with the hard-spheres approximation would yield a dependence of $T^{1.5}$. The calculated values of the diffusion coefficients of H_2SO_4, dimethylamine- and trimethylamine-sulfate in dry air at 298 K using the Fuller method are 0.11, 0.08 and 0.074 $cm^2\ s^{-1}$, respectively, which is in a reasonable agreement with our experimental data – the measured diffusion coefficient of H_2SO_4 at T=298 K under close to dry conditions (RH 4%) is 0.08 ($cm^2\ s^{-1}$). However, when calculating the diffusion coefficients of H_2SO_4 in dry air at lower temperatures (278 and 288 K) with the Fuller method, the agreement of the experimental values with the predictions deteriorates. The formula predicts significantly higher diffusion coefficients than those observed in the experiments. The calculated values of D_{AB} for H_2SO_4 are 0.104 $cm^2\ s^{-1}$ at T= 288 K and 0.098 $cm^2\ s^{-1}$ at T=278 K, and the measured values are 0.07 $cm^2\ s^{-1}$ at (T=288 K and RH=8 %) and 0.054 $cm^2\ s^{-1}$ at (T=278 K and RH=16 %), respectively. The temperature dependency of the experimental diffusion coefficients was found to be a power of 5.4 for the whole dataset and temperature range. Since the data show a clear stepwise temperature dependency we provide also two separate fits to data from 278 to 288 K and from 288 to 298 K, with power dependencies of 2.2 and 8.7, respectively. These numbers are striking when compared to the empirical method of Fuller et al. (1966), who obtained the best fit to 340 experimental diffusion coefficients with the power dependency of $T \propto 1.75$.

In Figure 5 we show the temperature dependency of the experimental data obtained from literature (Lovejoy and Hanson, 1996; Pöschl et al., 1998; Hanson and Eisele, 2000), predictions of the Fuller method for the diffusion coefficients of sulfuric acid, dimethylamine- and trimethylamine-sulfates in dry air, results of the clustering kinetics simulations using quantum chemical data for several simulated systems (discussed below), and the experimental data of this work. The data collected from literature, all obtained using laminar flow technique and N_2 as the carrier gas, show a temperature dependency opposite to the one expected from theory. However,

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306 the range of temperatures at which the measurements were carried out is quite narrow (only 8 K)
307 and different experimental set-ups could explain such behaviour.

308 The origin of the discrepancy in the temperature dependency of the diffusion coefficient in our
309 experiment remains unclear; however, a possible explanation could be the increased clustering of
310 H_2SO_4 at lower temperatures (see explanation below) with unavoidably present trace impurities
311 in the system, such as amines. The CIMS was used to measure the concentrations of H_2SO_4 gas
312 phase monomers and dimers during the experiments; larger clusters were outside the mass range
313 of the CIMS used. In order to explain the experimental observation of the temperature
314 dependency of the diffusion coefficient, the dimer to monomer ratio at different temperatures
315 was investigated. The H_2SO_4 dimer formation is a result of H_2SO_4 monomer collisions, and thus
316 the observed H_2SO_4 dimer CIMS signal depends on the H_2SO_4 monomer concentration and also
317 on the residence time, which determinates the time available for the clustering to take place
318 (Petäjä et al., 2011). No significant temperature dependency of the [dimer]/[monomer] ratio was
319 observed in our experiments, which is in agreement with Eisele and Hanson (2000), who report a
320 relatively constant H_2SO_4 [dimer]/[monomer] ratio with lowering temperature (the temperature
321 range investigated in their study was 235 – 250 K). On the other hand, they report a substantial
322 increase in the larger clusters' (trimer and tetramer) concentration with decreasing temperature
323 while the monomer concentration was almost constant. There are only a very few previously
324 reported values of the sulfuric acid dimer to monomer ratio from laboratory experiments. Petäjä
325 et al. (2011) studied the close to collision-limited sulfuric acid dimer formation under
326 experimental conditions similar to our study (T=293 K, RH=22 %, initial H_2SO_4 concentrations
327 from 10^6 to 10^8 molecule cm^{-3} with saturator containing liquid H_2SO_4 and in-situ H_2SO_4 using
328 O_3-photolysis as methods for producing gas phase H_2SO_4). They reported H_2SO_4
329 [dimer]/[monomer] ratios ranging from 0.05 to 0.1 at RH = 22 % and a residence time of 32 s.
330 Petäjä et al. (2011) speculate about the presence of a third stabilizing compound, and their
331 experimental dimer formation rates correspond well to modelled rates at a DMA concentration
332 of about 5 ppt. Almeida et al. (2013) reported [dimer]/[monomer] ratios from 0.01 to 0.06 for the
333 experiments in CLOUD chamber with addition of DMA (3-140 ppt, with the effect saturated for
334 addition >5 ppt) and [dimer]/[monomer] ratios from 1×10^{-4} to 0.003 for pure binary H_2SO_4-
335 water system, both at RH=38 % and T=278 K. In our measurements the H_2SO_4
336 [dimer]/[monomer] ratio under conditions T=298 K, RH=24 % and a residence time of ~37 s,
337 spans the range from 0.03 to 0.11, which is in reasonable agreement with values reported by both

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Petäjä et al. (2011) and Almeida et al. (2013) when trace impurity levels of DMA are present in the system.

The cluster population simulations using quantum chemical data (see Figs. 5, 6 and Table 1) show that the presence of base impurities may decrease the effective H_2SO_4 diffusion coefficient by attachment of base molecules to the acid. Simulations considering only hydrated H_2SO_4 molecules and no bases give higher values for the diffusion coefficient, and also a notably less steep temperature dependency (Table 1). Similarly to experiment the stepwise behaviour of temperature dependency could be found when fits are performed separately for temperatures 278-288 K and 288-298 K, see Table 1. This demonstrates that temperature-dependent clustering may change the behaviour of the effective diffusion coefficient with respect to temperature. Results obtained by simulating clusters containing H_2SO_4 and DMA are closer to the experimental diffusion coefficient values than those obtained using H_2SO_4 and TMA. On the other hand, the power dependency shows a better agreement for the H_2SO_4–TMA system (see Table 1).The best agreement between the simulations and the experiment was found for the temperature 298 K. Also, changing the base concentration according to Eq. 3 shows a better performance than keeping the base concentration constant. Allowing the formation of clusters containing up to two H_2SO_4 and two base molecules has no significant effect. In principle, the larger clusters bind H_2SO_4 molecules and may thus increase the apparent diffusion coefficient, but here their effect is minor due to the relatively low initial H_2SO_4 concertation of 5×10^6 cm^{-3} used in the simulations. More analysis on the effects of the amines can be found in the work by Olenius et al. (2014).

The formation of particles inside the flow tube during the experiments was measured regularly using Ultrafine Condensation Particle Counter (UCPC model 3776, TSI Inc. USA) with the lower detection limit of 3 nm. The highest determined concentration of particles was approximately 2×10^4 yielding the maximum nucleation rate J of ~ 500 particles cm^3 s^{-1} at T=278 K and RH=60 % . Since the nucleation rate was increasing with decreasing temperature and elevated RH in the flow tube, the loss of gas phase sulfuric acid to the particles was more pronounced at temperatures of 288 and 278 K. The losses of H_2SO_4 to particles were minimal – units of percent (see e.g. Brus et al. 2011 and Neitola et al, 2015 for details) and cannot explain our experimental observation of increased H_2SO_4 diffusion coefficient temperature dependency. The additional losses of H_2SO_4 would lead to increased values of observed loss rate coefficient (k_{obs}) and subsequently to higher diffusion coefficient.

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4. Conclusions

We have presented measurements of sulfuric acid diffusion coefficient in air derived from the first-order rate coefficients of wall loss of H_2SO_4. The experiments were performed in a laminar flow tube at temperatures 278, 288 and 298 K, relative humidities from 4 to 70 %, under atmospheric pressure and at initial H_2SO_4 concentrations from 10^6 to 10^8 molec. cm^{-3}. The chemical ionization mass spectrometer (CIMS) was used to measure H_2SO_4 gas phase concentration at seven different positions along the flow tube. The wall losses were determined from the linear fits to experimental ln[H_2SO_4] as a function of axial distance in the flow tube. The losses of H_2SO_4 inside the flow tube were also simulated using a computational fluid dynamics model (CFD-FLUENT), in which the wall is assumed to be an infinite sink for H_2SO_4. The experimentally determined H_2SO_4 losses along the flow tube were in a very good agreement with profiles calculated using the FLUENT model, where experimentally obtained diffusion coefficients were used as an input. A maximum difference of ~7 % for experiments conducted at T=278, 288 and 298 K and in the whole RH range was found when compared to model. The results of the fluid dynamics model (CFD-FLUENT) also satisfactory confirm the assumption of fully developed laminar profile inside the flow tube and infinite sink boundary conditions on the wall for H_2SO_4 loss.

To explain an unexpectedly high power dependency of the H_2SO_4 diffusion coefficient on temperature observed in our system we accounted in our calculations for involvement of base impurities: dimethyl- (DMA) and trimethyl-amine (TMA). The semi-empirical Fuller formula (Fuller et al., 1966) was used to calculate the diffusion coefficients at dry conditions for solely H_2SO_4, and H_2SO_4 neutralized with amine bases, namely dimethyamine- and trimethylamine-sulfate. Further, a molecular cluster kinetics model (Olenius et al. 2014) with quantum chemical input data was used to simulate acid–base cluster formation that may lead to the observed behaviour. With the simulations we obtained an effective diffusion coefficient determined in the same way as in the experiments.

The experimental H_2SO_4 diffusion coefficients were found to be independent of different initial [H_2SO_4] and a wide range of total flow rates. The values of the diffusion coefficient were found to decrease with increasing relative humidity owing to stronger hydration of H_2SO_4 molecules. The observed power dependency of the experimental diffusion coefficients as a function of temperature was found to be of the order of 5.4 when the whole temperature range is accounted for which is in a clear disagreement with predictions from the Fuller method (Fuller et al., 1966)

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having a power dependency of 1.75. Since the experimental diffusion coefficients deviate more from the theory towards the lower temperatures of 278 and 288 K, we suggest that a plausible explanation for this discrepancy is involvement of impurities such as amines, capable of binding to acid molecules with the binding strength increasing with decreasing temperature. This hypothesis is qualitatively supported by clustering kinetics simulations performed using quantum chemical input data for H_2SO_4–dimethylamine and H_2SO_4–trimethylamine clusters. Our results indicate that the effective diffusion coefficient of H_2SO_4 in air exhibits a stronger temperature dependency than predicted from a theory that does not consider cluster formation, and neglecting this dependency might result in incorrect determination of residual H_2SO_4 concentration in laboratory experiments. More measurements are therefore needed to gain a better understanding of the temperature dependency of the H_2SO_4 diffusion coefficient and the formation of larger H_2SO_4 clusters.

Acknowledgement

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552 **Table 1.** Summary of simulated and experimental averages (unweighted over RH) of the
553 effective H_2SO_4 diffusion coefficients D (cm^2 s^{-1}) with standard deviations in parenthesis for
554 three temperatures 278, 288 and 298 K. The initial base concentration $[base]_{init}$ is set to be either
555 RH-dependent according to Eq. (3) or RH-independent, and the simulations consider clusters
556 containing up to one acid and one base molecule ("1×1") or two acid and two base molecules
557 ("2×2") as well as hydrates of the clusters. Power dependencies with respect to the temperature,
558 obtained as linear fits to the data, are also listed.

559

Impurities			*D* (*T*=278K)	*D* (*T*=288K)	*D* (*T*=298K)	Power dependency*
Base	**$[Base]_{init}$**	**Simulated clusters**				
DMA	(0.1xRH+4) ppt	1x1	0.064 (7%)	0.069 (7%)	0.077 (7%)	2.20/3.18/2.68
		2x2	0.067 (6%)	0.072 (6%)	0.079 (6%)	2.06/2.92/2.48
	Constant 5 ppt	1x1	0.067 (4%)	0.072 (4%)	0.080 (4%)	2.16/3.01/2.58
		2x2	0.069 (3%)	0.074 (4%)	0.081 (4%)	2.02/2.77/2.39
TMA	(0.1xRH+2) ppt	1x1	0.065 (7%)	0.071 (6%)	0.080 (4%)	2.40/3.53/2.95
		2x2	0.068 (6%)	0.073 (5%)	0.081 (4%)	2.16/3.04/2.59
	Constant 2 ppt	1x1	0.065 (2%)	0.071 (2%)	0.080 (1%)	2.41/3.52/2.95
		2x2	0.067 (2%)	0.073 (2%)	0.081 (1%)	2.15/3.04/2.58
Only SA hydrates			0.079 (4%)	0.084 (4%)	0.089 (4%)	1.67/1.67/1.67
Experiment, this work			0.051 (11%)	0.055 (11%)	0.074 (7%)	2.18/8.70/5.35

560 *power dependency given separately for the temperature ranges 278-288 K / 288-298 K / the
561 whole dataset temperature range (278-298 K), the same RH range is used for both simulations
562 and experiment.

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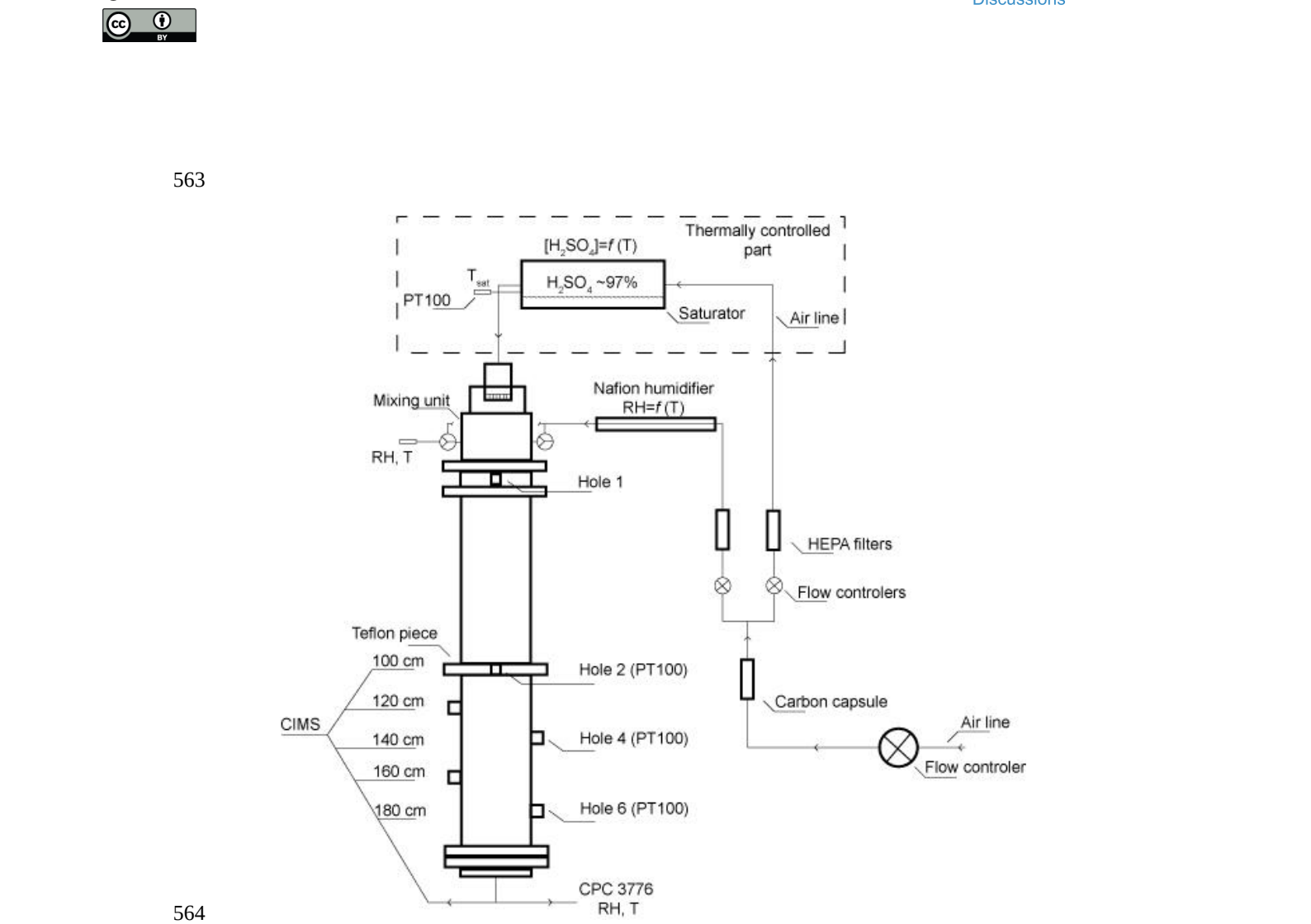

Figure 1. The schematic figure of the FMI flow tube.

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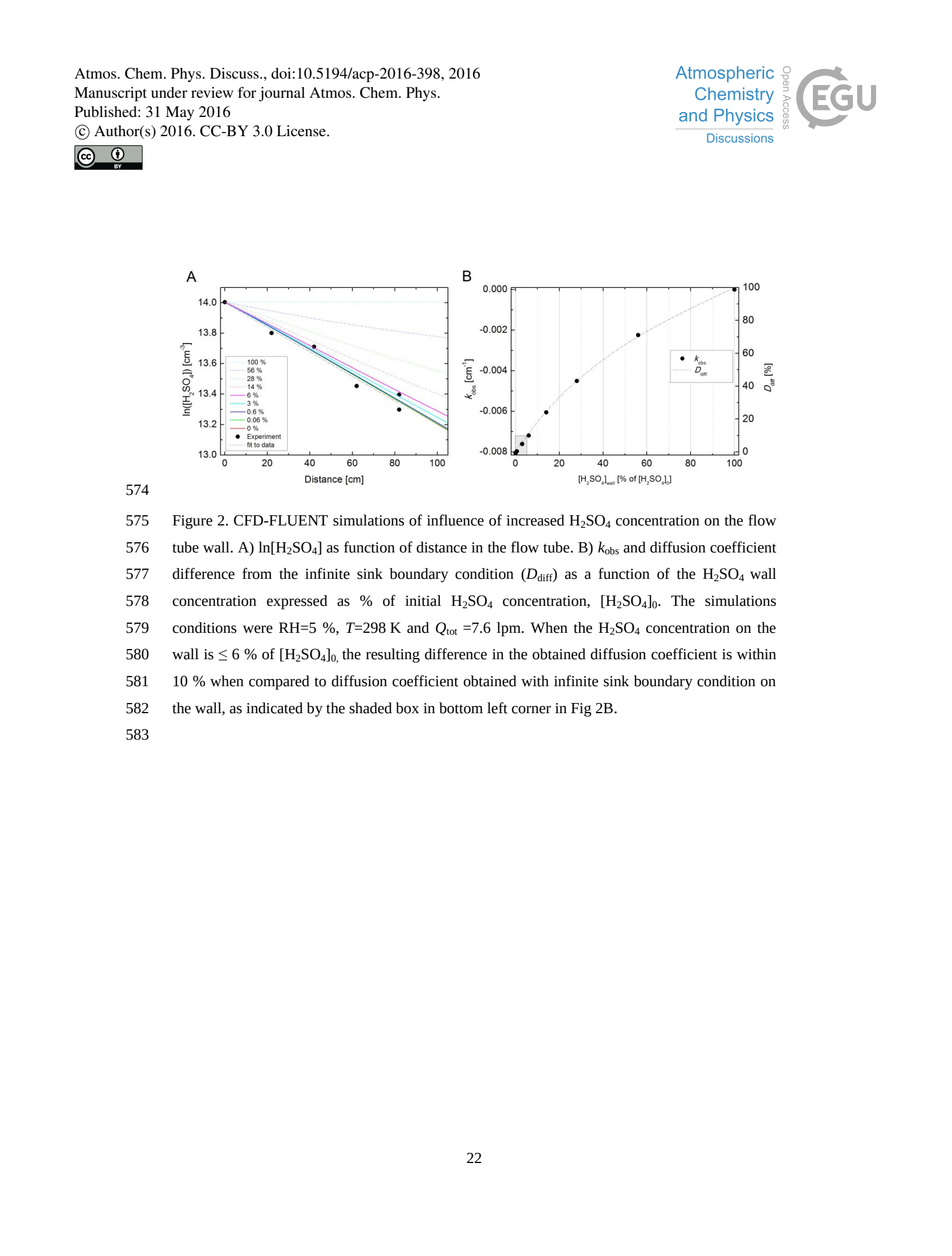

574

575 Figure 2. CFD-FLUENT simulations of influence of increased H_2SO_4 concentration on the flow
576 tube wall. A) ln[H_2SO_4] as function of distance in the flow tube. B) k_{obs} and diffusion coefficient
577 difference from the infinite sink boundary condition (D_{diff}) as a function of the H_2SO_4 wall
578 concentration expressed as % of initial H_2SO_4 concentration, $[H_2SO_4]_0$. The simulations
579 conditions were RH=5 %, T=298 K and Q_{tot} =7.6 lpm. When the H_2SO_4 concentration on the
580 wall is ≤ 6 % of $[H_2SO_4]_0$, the resulting difference in the obtained diffusion coefficient is within
581 10 % when compared to diffusion coefficient obtained with infinite sink boundary condition on
582 the wall, as indicated by the shaded box in bottom left corner in Fig 2B.
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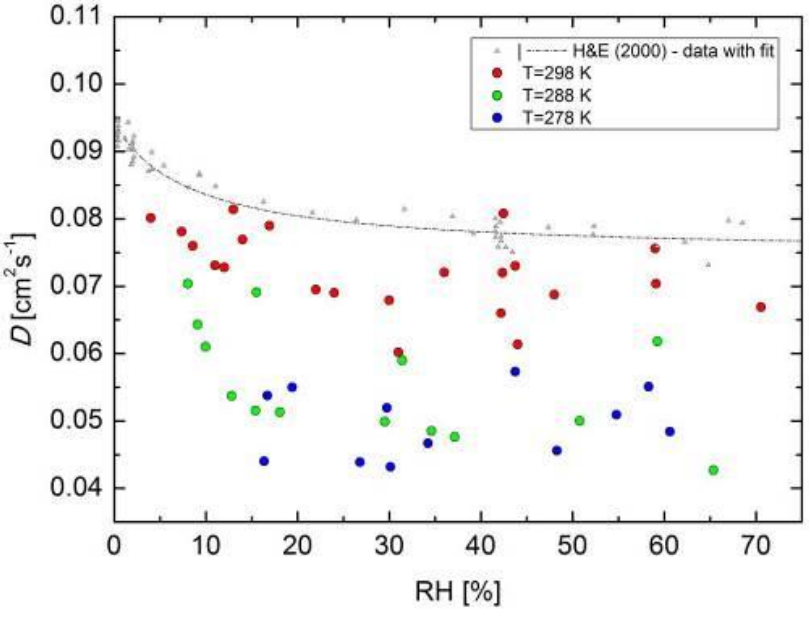

584

585 Figure 3. Experimental diffusion coefficient of H_2SO_4 in air as a function of relative humidity at
586 different temperatures compared with fit to the H_2SO_4 diffusion in N_2 data of Hanson and Eisele
587 (2000).

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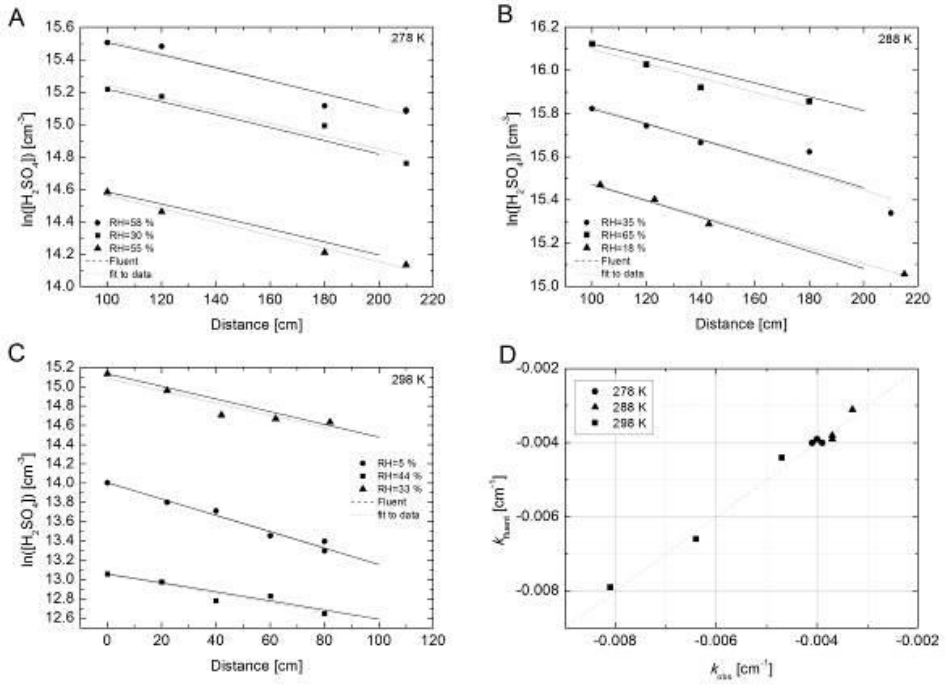

588

589 Figure 4. The sulfuric acid losses simulated with CFD-FLUENT model when the experimentally
590 obtained diffusion coefficients are used as an input at A) T=278 K B) T=288 K and C) T= 298 K.
591 D) simulated losses rate coefficients compared with experimental values of k_{obs} (cm^{-1}) at T=278,
592 288 and 298 K.

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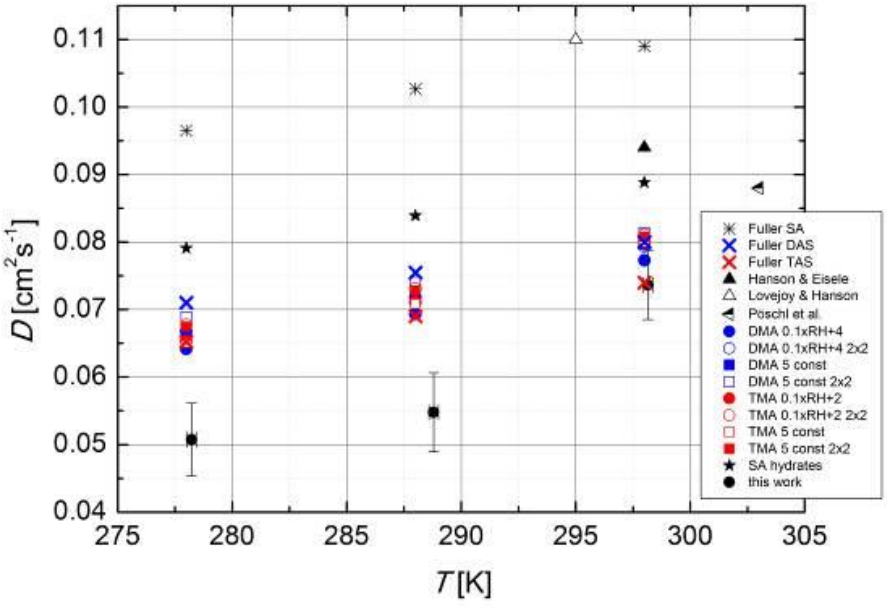

593

594 Figure 5. The temperature dependency of the effective H_2SO_4 diffusion coefficient, calculated
595 using the Fuller method for dry H_2SO_4 (SA), dimethylamine- (DAS) and trimethylamine-sulfate
596 (TAS), both in dry air, data from literature, several assemblies of cluster population simulations
597 (see text for details) and data measured experimentally in this work. The temperature
598 dependency of the experimental diffusion coefficients was found to be a power of 6.

599

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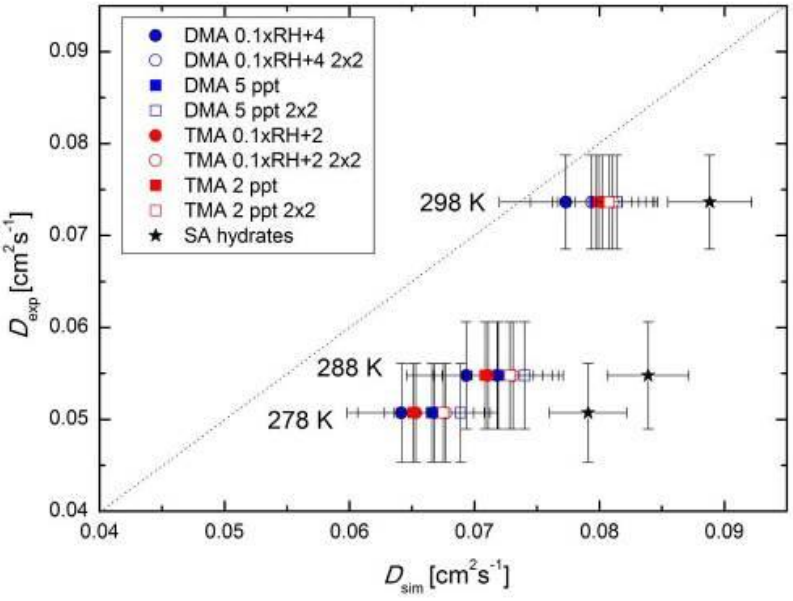

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601 Figure 6. Comparison of the experiment and the cluster population simulations at different
602 temperatures, considered are also different levels and sources of impurities in the system. The
603 formation of clusters containing up to two H_2SO_4 and two base molecules is denoted as "2×2" in
604 the legend.

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