IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.21 HET_SL_21

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$H_2SO_4 + H_2SO_4$ (aqueous) → 2 H_2SO_4 (aqueous)

Experimental data

Parameter	[H_2SO_4] /wt %	Temp./K	Reference	Technique/ Comments
Accommodation coefficient: α_b				
0.02-0.09	43	298	Van Dingenen and Raes, 1991	(a)
> 0.4	73-98	303	Pöschl et al., 1998	CWFT-CIMS (b)
0.96 ± 0.14	7-40	295	Hanson, 2005	AFT-CIMS (c)
0.76 ± 0.05	47-65			

Comments

(a) Uptake of H_2SO_4 was derived from particle growth measurements in a 230 L spherical batch reactor. Particle size distributions were measured with a differential mobility analyser. Seed H_2SO_4 particles were first produced by reaction of SO_2 with OH. OH was produced by photolysis of a NO_x mixture, thus likely from photolysis of HONO formed on the chamber walls. Loss of these particles within the reactor was then measured under dark conditions. Growth of the particles was observed in a third stage by again inducing H_2SO_4 formation as before, but with higher light intensity, resulting in growth of H_2SO_4 particles due to condensation of H_2SO_4. OH concentrations were estimated from the decay of the ratio of the concentrations of propene and propane also added to the reactor. The estimated OH level was used to infer the H_2SO_4 concentrations. When deriving the bulk accommodation coefficient from the growth rates, the Fuchs-Sutugin correction factor was used to account for gas phase diffusion.

(b) Coated wall flow tube operated at 0.5 – 10 Torr with CIMS detection of H_2SO_4 after reaction with SF_6^-. H_2SO_4 was delivered from a thermostated reservoir kept at 348 K. The reactor wall was coated by a thin H_2SO_4 film, the composition of which was determined by the H_2O pressure. The uptake coefficient (interpreted as bulk accommodation coefficient) was determined by fitting the first order loss rates taking into account gas phase diffusion. The best fit was obtained for a value of 0.65. Taking into account the uncertainties led to the lower limit listed in the table.

(c) Uptake to sulphuric acid aerosol was studied in a laminar flow reactor coupled to CIMS detection using HNO_3 as source of primary ions. Sulfuric acid particles were generated by homogeneous nucleation from supersaturated vapour leading to a lognormal particle size distribution within 50-120 nm, with a few 10^4 particles per cm^3, characterised by a differential mobility analyzer. Gas-phase sulphuric acid was generated by reaction of OH with SO_2 leading to concentrations of 3×10^9 cm^{-3} in the flow tube. This concentration is at least two orders of magnitude above the vapour pressure of sulphuric acid. Uptake to the particles did not lead to

significant growth. The measured uptake coefficients were corrected for gas phase diffusion using the Fuchs-Sutugin correction factor. The diffusion coefficient was directly measured based on the observed wall loss rates in absence of aerosol particles. Its negative humidity dependence was in line with previous measurements by Hanson and Eisele (2000).

Preferred Values

Parameter	Value	T/K
α_b, $[H_2SO_4] < 50$ wt%	1	200 – 300
α_b, $[H_2SO_4] > 50$ wt%	>0.7	200 – 300
Reliability		
$\Delta \log (\alpha_b)$	0.3	200 – 300

Comments on Preferred Values

Of the two more recent studies, the aerosol flow tube study by Hanson (2005) is much less affected by gas phase diffusion and can thus more reliably return high uptake coefficients. The slight trend for a lower bulk accommodation coefficient apparent in Hanson's data is not significant enough to provide a parameterized expression for the composition dependence. It is thus reflected by providing a lower limit of 0.7 for solutions >50 wt%. The coated wall flow tube study by Pöschl et al. is in agreement with these high values for α_b, keeping in mind that the wall loss rates were practically in the diffusion limit of that experiment. The earlier estimate of α_b based on particle growth measurements certainly suffered from the fact that neither the concentration of H_2SO_4 nor that of its precursor SO_2 was directly measured. In addition, the condensation rate derived was very sensitive to the wall loss rate of particles, which had to be determined in a separate experiment.

References

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