

# IUPAC Task Group on Atmospheric Chemical Kinetic data Evaluation – Data Sheet VI.A4.11 HET\_SL\_11

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## N<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O (aqueous sulphuric acid aerosol)

### Experimental data

Parameter	RH/ %	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients:</i>				
$\gamma, \gamma_{ss}, \gamma_0$				
0.10 ± 0.01	1-10 RH	293	Mozurkewitch and Calvert,	AFT-CL (a)
0.139 ± 0.009	1-10	274	1988	
0.12±0.03	40% H <sub>2</sub> SO <sub>4</sub>	226	Hanson and Ravishankara,	WWFT-
0.14±0.03	60% H <sub>2</sub> SO <sub>4</sub>		1991a	CIMS
0.10±0.02	70% H <sub>2</sub> SO <sub>4</sub>			(b)
0.10±0.02	75% H <sub>2</sub> SO <sub>4</sub>			
0.058±0.006	73% H <sub>2</sub> SO <sub>4</sub>	283	Van Doren et al., 1991	DT-TDLAS
				(c)
0.055±0.010	74%-96% H <sub>2</sub> SO <sub>4</sub>	220±5	Golden et al., 1992; Williams et al., 1994; Manion et al., 1994	Knud-MS (d)
0.06±0.04	79-84% H <sub>2</sub> SO <sub>4</sub>	293	Fried et al., 1994	AFT-CL(e)
0.103±0.006	64-81%	273		
0.12±0.016	57-76%	260		
0.148±0.011	63-76%	247		
0.086±0.009	61-63%	247		
0.146±0.036	69-71%	230-234		
0.102±0.011	65-69%	231-234		
0.077±0.019	54-64%	225-231		
0.076±0.018	60% H <sub>2</sub> SO <sub>4</sub>	270	Hanson and Lovejoy, 1994	AFT-
0.081±0.032	60% H <sub>2</sub> SO <sub>4</sub>	230		CIMS(f)
0.061±0.013	70% H <sub>2</sub> SO <sub>4</sub>	296		
0.109±0.024	70% H <sub>2</sub> SO <sub>4</sub>	230		
0.077±0.016	80% H <sub>2</sub> SO <sub>4</sub>	270		
0.090±0.020	80% H <sub>2</sub> SO <sub>4</sub>	230		
0.11	53% H <sub>2</sub> SO <sub>4</sub>	200	Zhang, Leu and Keyser,	WWFT-
0.034	29%	195	1995	CIMS
0.021	H <sub>2</sub> SO <sub>4</sub> ,16.4%HN	200		(g)
0.045	O <sub>3</sub>	200		
0.10	5% H <sub>2</sub> SO <sub>4</sub> ,41% HNO <sub>3</sub> 40% H <sub>2</sub> SO <sub>4</sub> ,10% HNO <sub>3</sub> 5% H <sub>2</sub> SO <sub>4</sub> ,41% HNO <sub>3</sub>	220		
0.075±0.047	65% H <sub>2</sub> SO <sub>4</sub>	210-230	Beichert and Finlayson- Pitts, 1996	Knud-MS (h)
0.023 ± 0.004	90 % RH, 17%	297	Hu and Abbatt, 1997	AFT-
0.038 ± 0.012	H <sub>2</sub> SO <sub>4</sub>			CIMS/OPC
0.060 ± 0.020	58.5% RH, 40%			(i)

0.050 ± 0.008	H <sub>2</sub> SO <sub>4</sub> 19.5% RH, 59% H <sub>2</sub> SO <sub>4</sub> 8.5% RH, 66% H <sub>2</sub> SO <sub>4</sub>				
0.187 ± 0.028	69% H <sub>2</sub> SO <sub>4</sub>	240	Robinson et al., 1997	DT-TDLAS	
0.154 ± 0.023	69% H <sub>2</sub> SO <sub>4</sub>	260		(j)	
0.159 ± 0.024	39% H <sub>2</sub> SO <sub>4</sub>	231			
0.086 ± 0.0129	39% H <sub>2</sub> SO <sub>4</sub>	255			
0.11 ± 0.02	60% H <sub>2</sub> SO <sub>4</sub>	210-230	Hanson, 1997	WWFT and	
0.092	55%	202		AFT-	
0.021	H <sub>2</sub> SO <sub>4</sub> ,5%HNO <sub>3</sub>			CIMS(k)	
0.045	45%	230			
0.10	H <sub>2</sub> SO <sub>4</sub> ,15%HNO <sub>3</sub> 59%H <sub>2</sub> SO <sub>4</sub> ,0.08% HNO <sub>3</sub> 58% H <sub>2</sub> SO <sub>4</sub> ,1-2% HNO <sub>3</sub>				
0.033 ± 0.004	8-80% RH, 26.3- 55% H <sub>2</sub> SO <sub>4</sub>	298 298	Hallquist et al., 2000	AFT- CL/SMPS (l)	
0.028 ± 0.008	40% RH, 49%	288			
0.036 ± 0.004	H <sub>2</sub> SO <sub>4</sub>	278			
0.049 ± 0.009	40% RH,	268			
0.091 ± 0.019	48%H <sub>2</sub> SO <sub>4</sub>	263			
0.092 ± 0.013	40% RH, 44% H <sub>2</sub> SO <sub>4</sub> 40% RH, 42% H <sub>2</sub> SO <sub>4</sub> 40% RH, 42%				
0.045	H <sub>2</sub> SO <sub>4</sub> 0.7 % RH, 81%	295±1	Kane et al., 2001	AFT- CIMS/SMPS	
0.045 ± 0.013	H <sub>2</sub> SO <sub>4</sub>			(m)	
0.030	2.9 % RH, 76%				
0.075	H <sub>2</sub> SO <sub>4</sub>				
0.061	7.7 % RH, 70% H <sub>2</sub> SO <sub>4</sub> 16 % RH, 63% H <sub>2</sub> SO <sub>4</sub> 28.4 % RH, 55% H <sub>2</sub> SO <sub>4</sub>				
0.050	38± 2% H <sub>2</sub> SO <sub>4</sub>	193.6	Wagner et al., 2005	Static	
0.044	32%			Reactor-FTIR	
0.033	H <sub>2</sub> SO <sub>4</sub> ,10%HNO <sub>3</sub>			(o)	
0.016	17% H <sub>2</sub> SO <sub>4</sub> ,34%HNO <sub>3</sub> 9% H <sub>2</sub> SO <sub>4</sub> ,48% HNO <sub>3</sub> 58% H <sub>2</sub> SO <sub>4</sub> ,1-2% HNO <sub>3</sub>				

### Comments

- (a) Atmospheric pressure aerosol flow tube with N<sub>2</sub>O<sub>5</sub> ( $\approx 10^{13}$  molecule cm<sup>-3</sup>) measured by a modified chemiluminescence method, via thermal dissociation to NO<sub>3</sub> and titration with NO, which was detected. Aerosols generated in a constant output atomiser, dried, and size selected with a differential mobility analyser (DMA) coupled to a condensation particle counter (CPC).

The monodisperse aerosol was then equilibrated at controlled humidity before entry into the flow tube. The typical diameter,  $d_{\text{mean}}$  was 0.08-0.2  $\mu\text{m}$ , with surface area density of  $1 - 5 \times 10^{-5} \text{ cm}^2/\text{cm}^3$ . Uptake coefficients were determined from the first order rate constants for  $\text{N}_2\text{O}_5$  decay, corrected for wall loss, which were linearly dependent on surface area. Diffusion limitation was negligible for the size range used. The uptake of  $\text{N}_2\text{O}_5$  on  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  was independent of RH in the range 1-10%.

- (b) Wetted wall flow tube coupled to CIMS detection. Aqueous  $\text{H}_2\text{SO}_4$  film residence time of 20-30s.  $P(\text{H}_2\text{O})$  was  $\sim 1.3 \times 10^{-3}$  mbar. The temperature dependence of  $\gamma$  was measured for the 60% and 70%  $\text{H}_2\text{SO}_4$  solution: none was found within the reported error limits.
- (c) Fast train of 200 $\mu\text{m}$  73%  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  droplets traversing a flow tube with TDLAS detection. Pressures = 13.3 mbar and droplet-gas interaction times of 1-2 ms.
- (d) Knudsen cell technique using MS detection.  $P(\text{N}_2\text{O}_5)$  was 0.4 to  $10 \times 10^{11}$  molecule  $\text{cm}^{-3}$ .  $\gamma$  value of 0.02-0.03 -independent of temperature, concentration (74 to 96%  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ).  $\gamma$  value corrected for saturation effects.
- (e) High pressure (0.3 to 0.8 atm) flow tube using slow flow conditions and sub micron  $\text{H}_2\text{SO}_4$  aerosol generated by homogeneous nucleation from the reaction of  $\text{SO}_3 + \text{H}_2\text{O}$ . Particle size 60 - 250 nm diameter at 225 to 293K, with  $\text{H}_2\text{SO}_4$  54 to 82wt%.  $\text{N}_2\text{O}_5$  (30 to 200 ppb) detected by titrating with NO in a heated quartz tube, using TDLAS to monitor NO and also  $\text{H}_2\text{O}$  vapor.
- (f) Kinetics of  $\text{N}_2\text{O}_5$  hydrolysis on sulfuric acid aerosol measured in laminar flow reactor at 825 mbar of  $\text{N}_2$ , using CIMS detection. The aerosol surface area was determined by UV extinction using Mie theory. The  $\text{H}_2\text{SO}_4$  particle concentration were in the range 5 -  $100 \times 10^4$  particles  $\text{cm}^{-3}$  with diameters between 0.2 to 0.4  $\mu\text{m}$ . Initial  $\text{N}_2\text{O}_5$  concentration was of the order of 1 to  $5 \times 10^{13}$  molecule  $\text{cm}^{-3}$ . The uptake measurements on 60%  $\text{H}_2\text{SO}_4$  at 230 K may have been influenced to some extent by  $\text{HNO}_3$  uptake and hence partial saturation.
- (g) Wetted wall flow reactor - CIMS. Liquid sulfuric acid films were applied to the cooled wall of a horizontally mounted tube. Total pressure = 0.53 mbar of He with partial pressure of  $\text{N}_2\text{O}_5$  of  $6.7 \times 10^{-7}$  mbar. The  $\gamma$  values decrease with increasing  $\text{HNO}_3$  content hence decreasing temperature at constant  $\text{H}_2\text{O}$  and  $\text{HNO}_3$  partial pressure. On the binary  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  surface  $\gamma=0.1$  independent of temperature. In the temperature range 195 to 220 K  $\gamma$  may be expressed as  $\gamma = -0.379 + 0.00213T$  at  $P_{\text{H}_2\text{O}} = 5 \times 10^{-7}$  mbar and  $P_{\text{HNO}_3} = 6.7 \times 10^{-7}$  mbar.
- (h) Knudsen flow reactor using MS detection.  $\text{N}_2\text{O}_5$  concentration was in the range 3 to  $90 \times 10^{11}$  molecule  $\text{cm}^{-3}$ .
- (i) Atmospheric pressure aerosol flow tube with detection of  $\text{N}_2\text{O}_5$  ( $7 \times 10^{12}$  molecule  $\text{cm}^{-3}$ ) by CIMS using  $\text{I}^-$  reagent ion. The aerosols were generated in an ultrasonic nebuliser and were equilibrated with the ambient humidity before entry into the flow tube. The size distribution, measured with an optical particle counter (OPC), was used to calculate the surface area of the aerosol in the flow tube. The peak in the surface area distribution,  $d_{\text{max}}$  was between 2 and 4  $\mu\text{m}$ . The counter was calibrated by collection of aerosol of known composition in a aqueous trap (assumed 100% efficient) and measurement of the electrical conductivity of the trapped electrolyte. Uptake coefficients were determined from the first order rate constants for  $\text{N}_2\text{O}_5$  decay, corrected for wall loss (Brown correction), and for diffusion limitation to the particle surface assuming an average diameter,  $d_{\text{max}}$ , of the non-monodisperse aerosol. The first order rate constant for the title reaction scaled linearly with the aerosol surface area. Cited errors on  $\gamma$  is  $\pm 1\sigma$  precision; the estimated potential systematic error arising mainly from measurement of the SA was  $\pm 25\%$ .  $\text{HNO}_3$  accumulation in the aerosol was insignificant.
- (j) Fast train of 200 $\mu\text{m}$   $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  droplets traversing a flow tube with TDLAS detection. Pressures = 13.3 mbar and droplet-gas interaction times of 2 to 20 ms. The temperature of the droplets was inferred from the water partial pressure measured by TDL absorption. A negative temperature dependence of  $\gamma_{\text{SS}}$  was observed for  $T \geq 230\text{K}$  and  $\gamma_{\text{SS}}$  slightly increased with increasing concentration of  $\text{H}_2\text{SO}_4$  measured at 39, 54 and 69%. Model involving neutral and acid catalysed mechanism for  $\text{N}_2\text{O}_5$  hydrolysis fitted data from several laboratories.

- (k) Flow reactors with sulfuric acid wall film (0.2 mm thickness) and sub-micron aerosol (particle size 0.1 $\mu$ m) - CIMS detection. The pressure was 0.5 mbar He in the wall coated tube and 240 mbar of N<sub>2</sub> in the aerosol flow tube. Initial [N<sub>2</sub>O<sub>5</sub>] was 5 x 10<sup>11</sup> molecule cm<sup>-3</sup> for the aerosol and 5 x 10<sup>11</sup> molecule cm<sup>-3</sup> for the bulk liquid experiment.
- (l) Uptake study using a sulfuric acid aerosol of typically 1.5 to 4x10<sup>5</sup> particles cm<sup>-3</sup> of 240 to 400 nm peak diameter flowing down a laminar flow tube and interacting with N<sub>2</sub>O<sub>5</sub> whose concentration was in the range 2.5-12.5 x 10<sup>12</sup> cm<sup>-3</sup>. The  $\gamma$  value is independent of rh at 298 K and has a strong negative temperature dependence at approximately 45%wt in the stated range. The reaction mechanism is complex and is controlled by competing reactions of direct and acid-catalyzed hydrolysis whereas ionic dissociation of N<sub>2</sub>O<sub>5</sub> into NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>+</sup> does not seem to play a role at low temperatures.
- (m) Atmospheric pressure flow tube with contact times between 1.5 and 7s once the 100nm diameter aerosol was well mixed with N<sub>2</sub>O<sub>5</sub> that was detected using CIMS. The  $\gamma$  value increased monotonously to  $\gamma = 0.05 \pm 0.025$  at 100%rh for both ammonium salts which was identical to the average value for the uptake of N<sub>2</sub>O<sub>5</sub> on H<sub>2</sub>O at 300K.
- (n) N<sub>2</sub>O<sub>5</sub> uptake experiment in an aerosol flow tube at characteristic N<sub>2</sub>O<sub>5</sub> concentrations of 500ppb coupled to NO<sub>2</sub> detection using a chemiluminescence detector after thermal decomposition of N<sub>2</sub>O<sub>5</sub> and following NO<sub>3</sub> titration with NO. Typical aerosol number densities were (6-10)x10<sup>5</sup> particles cm<sup>-3</sup>. The  $\gamma$  values were independent of RH in the range 8 - 80%, and hence on aerosol H<sub>2</sub>O content in the range 24.3 - 64.5wt% H<sub>2</sub>SO<sub>4</sub>.  $\gamma$  showed a negative temperature dependence at RH = 40%.
- (o) Uptake of N<sub>2</sub>O<sub>5</sub> prepared in situ in a large aerosol cold chamber (AIDA) equipped with aerosol metrology instrumentation, gas-and particular phase H<sub>2</sub>O detection using hygrometers and FTIR extinction measurement capabilities. Saturated ternary solutions (STS) consisting of H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>/H<sub>2</sub>O were formed by the interaction of N<sub>2</sub>O<sub>5</sub> between the initial 38 wt% H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O background aerosol with H<sub>2</sub>O vapour from ice-coated chamber walls. The decrease of  $\gamma$  with increasing mixing ratio of HNO<sub>3</sub> is attributed to the nitrate effect at low temperatures.

### Preferred Values

Parameter	Value	T/K
$\alpha$	0.042	298
$\alpha$	$2.3 \times 10^{-5} \cdot \exp(2240/T)$	240 -300
$\gamma$	$[(7353/T) - 24.83]^{-1}$	210 - 300
<i>Reliability</i>		
$\Delta \log (\alpha)$	$\pm 0.1$	298
$\Delta \log (\gamma)$	$\pm 0.3$ at 50% RH	260 -305

### Comments on Preferred Values

There is a large body of experimental data on the uptake of N<sub>2</sub>O<sub>5</sub> on H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O surfaces covering the wide range of temperature and humidity relevant for the atmosphere between the surface and the lower stratosphere. The results are generally consistent between the different studies which used both bulk and dispersed (aerosol) surfaces. At room temperature  $\gamma$  shows little dependence on RH in the range 8 - 80%, and hence on aerosol H<sub>2</sub>O content in the corresponding range 20 - 70 wt% H<sub>2</sub>SO<sub>4</sub>. However at low temperatures there is a fall off in  $\gamma$  with decreasing water content.  $\gamma$  shows a distinct negative temperature dependence at T > 230

K, but at lower temperature the temperature dependence becomes positive. The uptake leads to hydrolysis of N<sub>2</sub>O<sub>5</sub> and formation of HNO<sub>3</sub> which transfers to the gas phase. However at low temperatures the increased solubility of HNO<sub>3</sub> in the H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O particles leads to a reduction in the uptake rate.

The lack of a dependence on the water content of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O surfaces and the negative temperature dependence at T>230 K suggests that uptake is controlled by a surface process, either mass accommodation or surface reaction. It is suggested by Robinson et al (1997) that the change in behaviour at low temperature is due to uptake under these conditions becoming limited by the rate of hydrolysis of N<sub>2</sub>O<sub>5</sub> in bulk liquid phase. They presented a phenomenological model which accounts for the observed dependence of the uptake coefficients on concentration and temperature. Two hydrolysis pathways are proposed, a direct reaction with H<sub>2</sub>O and an acid-catalysed reaction involving dissociation of N<sub>2</sub>O<sub>5</sub> promoted by H<sup>+</sup> ions.

The recommended expression for  $\gamma$  uses a resistance-model formulation but with an empirical representation of the temperature dependent liquid phase resistance due to chemical reaction,  $\gamma_r$ :

$$\gamma = \left\{ \frac{1}{\alpha_b} + \frac{1}{\gamma_r} \right\}^{-1}$$

The recommended value of  $\alpha_b$  is based on a linear least squares fit to all data at T>240 K, plotted in the form  $\ln[\alpha/(1-\alpha)]$  vs  $1/T$ . The temperature dependence of the  $\gamma_r$  term was determined by plotting the difference term  $(1/\gamma_{obs}-1/\alpha)$  against  $1/T$  and using linear regression to evaluate the empirical relationship between  $1/\gamma_r$  and temperature. Fig1 shows calculated uptake coefficients as a function of temperature compared with the experimental data determined for a range of [H<sub>2</sub>SO<sub>4</sub>].

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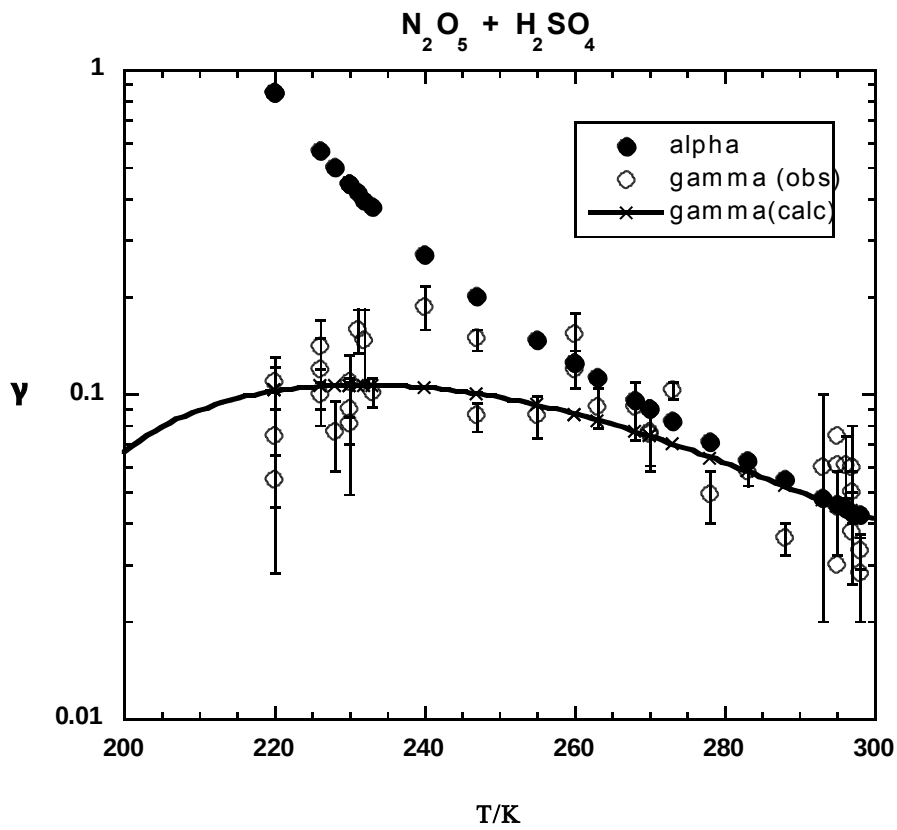


Figure 1: Uptake coefficients for uptake of  $\text{N}_2\text{O}_5$  by  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  aerosol plotted as a function of temperature. -X- recommended functional form; o = observations with error limits; filled circles: predicted accommodation coefficient from fit to data at  $T > 260$  K.

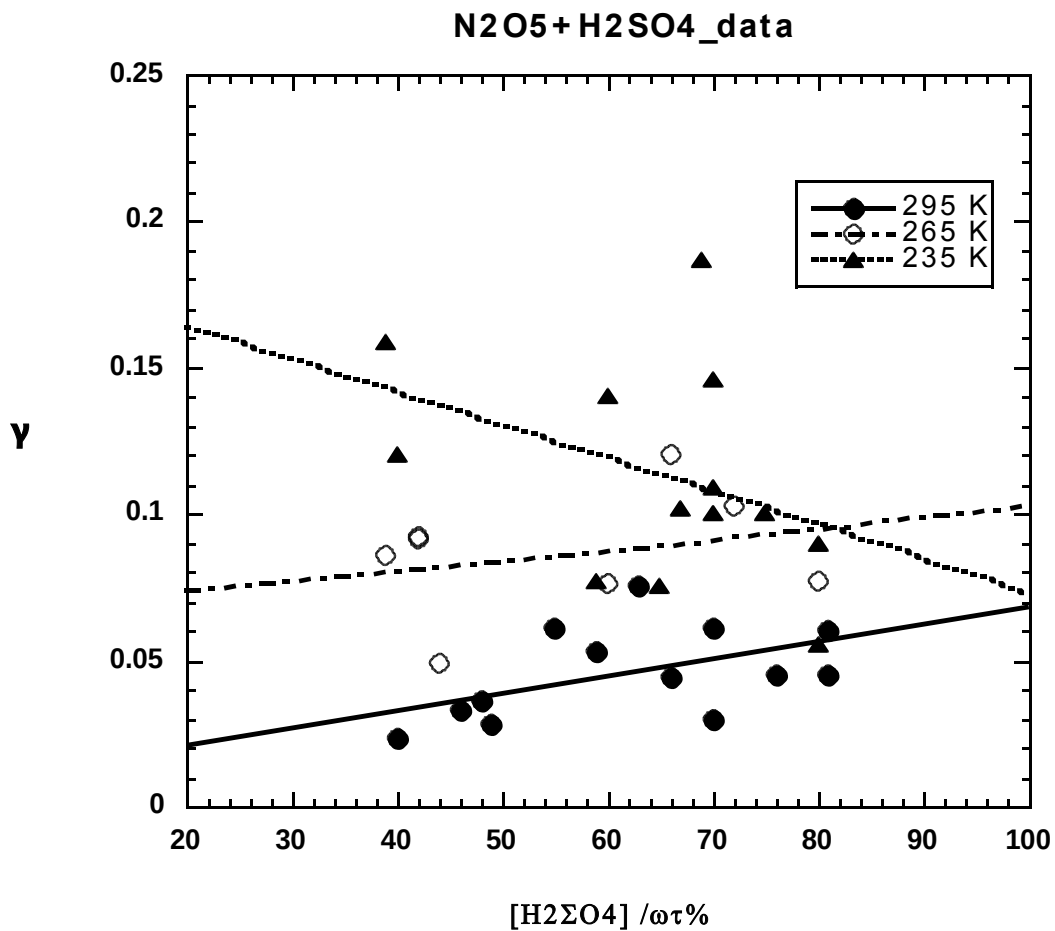


Figure 2: Uptake coefficients for uptake of N<sub>2</sub>O<sub>5</sub> by H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O aerosol plotted as a function of acid strength. Data selected in temperature range ± 10 K around 295, 265, and 235 K.



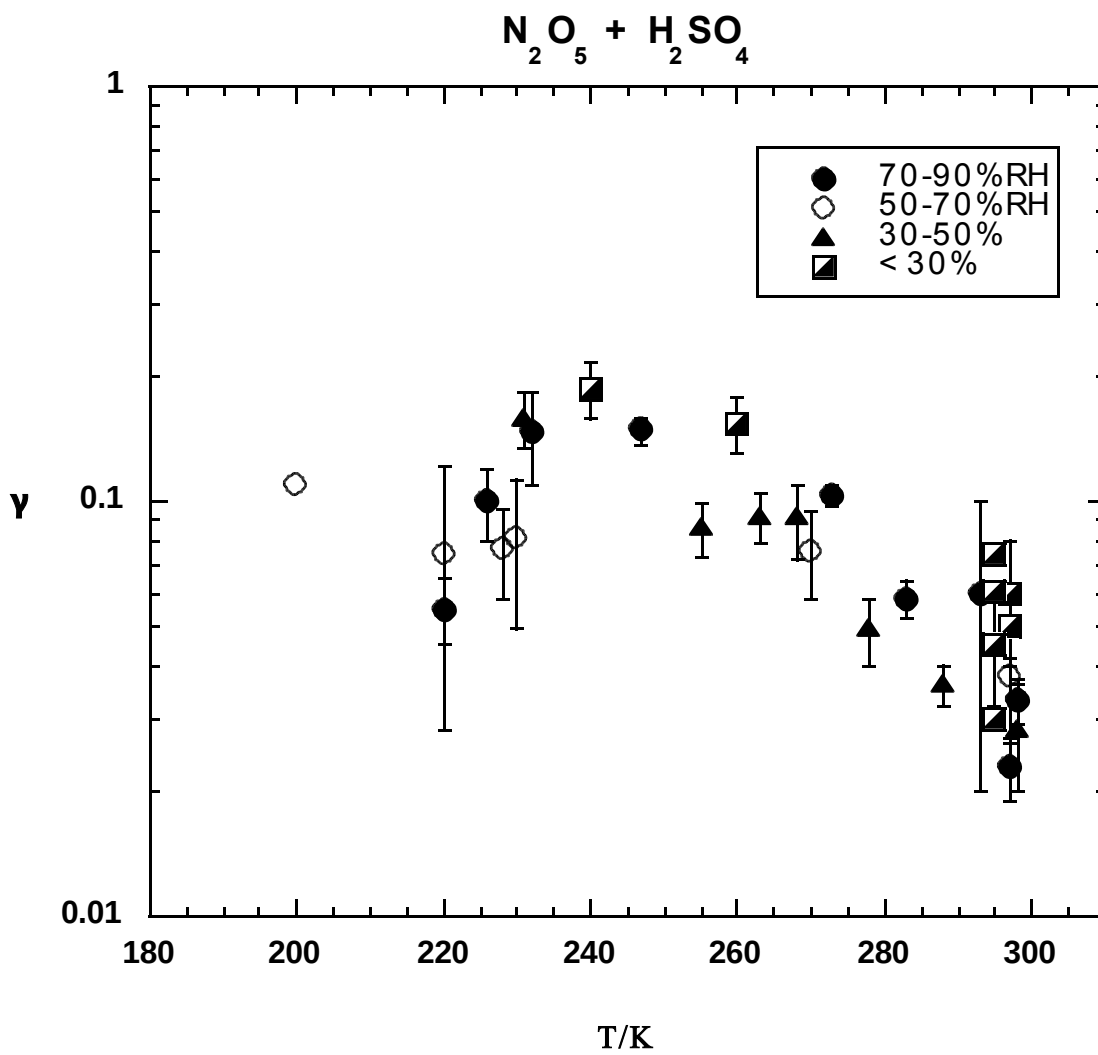


Figure 3: Uptake coefficients for uptake of  $\text{N}_2\text{O}_5$  by  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  aerosol plotted as a function of temperature. Data selected in RH range  $\pm 10\%$  around 80, 60, 40% and  $<30\%$  RH.

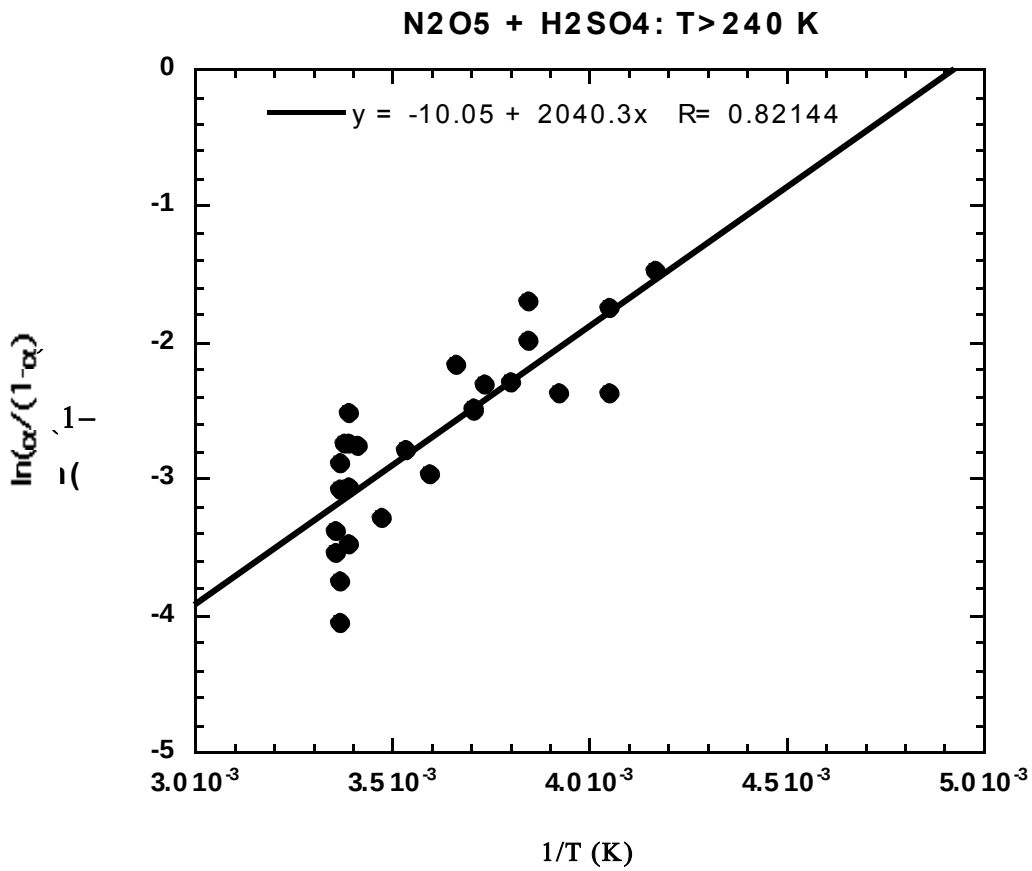


Figure 4: Uptake coefficients ( $\gamma = \alpha$ ) for uptake of  $\text{N}_2\text{O}_5$  by  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  aerosol plotted in functional form :  $\ln(\alpha/(1-\alpha))$  vs  $1/T$ . Data selected in temperature range 240 - 298 K.