IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.8 HET_SL_8

$HNO_3 + H_2SO_4 \rightarrow$ products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ			
$\gamma_{ss} = 2.0$ x 10^{-3} (75 wt % H_2SO_4)	230	Tolbert et al., 1988	Kn-MS (a)
$\gamma_{ss} = 4.0$ x 10^{-3} (96.5 wt % H_2SO_4)	295		
$\gamma = 0.28$ (5 wt % H_2SO_4)	188	Reihs et al., 1990	Kn-MS (b)
$\gamma = 0.25$ (40 wt % H_2SO_4)	188		
$\gamma = 0.12$ (58 wt % H_2SO_4)	188		
$\gamma = 0.07$ (74 wt % H_2SO_4)	188		
$\gamma = 0.05$ (83 wt % H_2SO_4)	188		
$\gamma = 0.001$ (96 wt % H_2SO_4)	188		
$\gamma = 0.07 \pm 0.01$ (15-66 wt % H_2SO_4)	223		
$\gamma = 0.015$ (74 wt % H_2SO_4)	223		
$\gamma = 0.003$ (87 wt % H_2SO_4)	223		
$\gamma = 0.11\pm0.01$ (73 wt % H_2SO_4)	283	Van Doren et al., 1991	DT-IR (c)
$\alpha_s > 0.8$ (70 wt % D_2SO_4)	213	Morris et al., 2000	MB (d)
$\alpha_b > 0.8$ (70 wt % D_2SO_4)			
Solubility: H			
H*= 3.56 x 10^{-3} exp(3320/T) (87 wt % H_2SO_4)	188-240	Reihs et al., 1990	(b)
H*= 8.54 x 10^{-3} exp(3550/T) (74 wt % H_2SO_4)			
H*= 2.02 x 10^{-1} exp(3190/T) (66 wt % H_2SO_4)			
H*= 7.47 x 10^{-8} exp(7160/T) (58 wt % H_2SO_4)			
(4 ± 1) x 10^3 M atm^{-1} (73 wt % H_2SO_4)	283	Van Doren et al., 1991	(c)
H*= 9.03 x 10^{-8} exp(7750/T) (40 wt % H_2SO_4)	190-230	Zhang et al., 1993	(e)
H*= 4.85 x 10^{-8} exp(7470/T) (50 wt % H_2SO_4)			
H*= 2.44 x 10^{-8} exp(7300/T) (60 wt % H_2SO_4)			
H*= 6.32 x 10^{-9} exp(7240/T) (70 wt % H_2SO_4)			
H*= 6.13 x 10^{-9} exp(7030/T) (75 wt % H_2SO_4)			

Comments

(a) The bulk substrate was cooled slowly to temperatures of 210 K to 230 K. The recovery yield of HNO_3 that was condensed at 230 K on 75% H_2SO_4 was approximately 20% in contrast to 100% for pure ice.

(b) The sulphuric acid substrate was prepared from bulk solutions and cooled to the temperature range 188 K to 240 K. γ was time dependent, the uptake coefficients given in the table are those measured after 100 s (the experiments spanning a total time of 2000 s). The time dependence was used to estimate the effective solubility assuming solubility limited uptake. The diffusion coefficient in the liquid phase was extrapolated from a room temperature value of 10^{-5} cm^{2}s^{-1} in 60% H_2SO_4 using

temperature dependent viscosity data from the literature. The error in H* is estimated to be a factor of 3. The expressions given in the table were obtained from fits to a Van't Hoff plot.

(c) Fast droplet train (73% H_2SO_4-H_2O droplets) traversing a flow tube. HNO_3 was detected by TDLAS. The γ values were corrected for gas-phase diffusion. The solubility was obtained by assuming that the measured uptake coefficient is due to solubility limited uptake. The bulk accommodation coefficient was assumed to be independent of H_2SO_4 concentration and similar to that of water (0.17). The liquid phase diffusion coefficient was estimated to be 9 x 10^{-7} cm^2 s^{-1} at 283 K based on the estimated temperature dependence of viscosity data.

(d) Molecular beam experiment with HNO_3 beam produced from the expansion of a 1% HNO_3 in H_2 mixture, leading to an incident HNO_3 energy 150 kJ/mol, hitting the 70.5% D_2SO_4 at 213 K. Fluxes were estimated to be below 10^{15} cm^{-2} s^{-1}. Scattered or desorbing molecules were detected with a mass spectrometer at an exit angle of 45°. A large fraction of incident HNO_3 molecules transfers their kinetic energy to the substrate; the inelastically scattered HNO_3 molecules lost 85% of their original energy on average. We use this as a lower bound to α_s reported in the table, even though the authors do not report the trapping probability for HNO_3. They argue that it is close to 1 at low, atmospherically relevant incident energies. 95% of those molecules trapped on the surface undergo proton exchange in the bulk of D_2SO_4. Therefore α_b is listed in the table with the same lower bounds.

(e) Static vapour pressure measurement of HNO_3 (MS) over a stirred H_2SO_4/HNO_3/H_2O solution.

Preferred Values

Parameter	Value	T/K
α_s	>0.8	188 - 223
α_b	>0.8	188 - 223
m_1 (wt.%$^{-2}$ K)	0.14	190-300
m_2 (wt.%$^{-1}$ K)	-36	190-300
m_3 (K)	8980	190-300
b_1 (wt.%$^{-2}$)	0.00063	190-300
b_2 (wt.%$^{-1}$)	0.012	190-300
b_3	14.7	190-300
Reliability		
$\Delta \log (\alpha_b)$	undetermined	
$\Delta \log (\alpha_s)$	undetermined	
$\Delta \log (H^*)$	0.5	190-300

Comments on Preferred Values

The molecular beam experiment by Morris et al. (2000) provides the most direct picture of HNO_3 interacting with the surface of sulphuric acid. Most of the HNO_3 molecules colliding with the surface are trapped, and nearly all of these undergo rapid proton exchange due to efficient solvation in the bulk. HNO_3 forms very stable complexes with H_2O and H_2SO_4 that may also be important for the stabilization of HNO_3 in the interfacial region (Yang and Finlayson-Pitts, 2001; Fairbrother and Somorjai, 2000). We therefore follow Morris et al. for recommending a lower limit to α_s and α_b.

In Knudsen cell and droplet train experiments, uptake of HNO_3 into H_2SO_4 solutions was time dependent and followed the behaviour expected for solubility limited uptake in the studies by Reihs et al. (1990) and Van Doren et al. (1991). The slow evaporation observed by Tolbert et al. (1988) with thermal desorption spectrometry appears to be consistent with this. Bulk accommodation was therefore not rate limiting the uptake. The decreasing trend with increasing sulphuric acid concentration reflects the increasing degree of solubility limitation at short interaction times. Initial uptake coefficients extracted from the time dependent traces are not reported that could be compared to the Morris et al. (2000) study.

Estimating Henry's Law constants from the time dependent uptake data carries a large uncertainty, as high experimental stability is required to allow reliable $t^{1/2}$ fits to the data and also due to the uncertainty associated with estimating the temperature dependent diffusion

coefficients. The solubility data extracted from the kinetic experiments by Reihs et al. (1990) and extrapolated to higher temperatures are consistent with vapour pressure measurements for the ternary HNO_3-H_2SO_4-H_2O system reported by Vandoni (1944) at 273 K. We use the Zhang et al. (1993) solubility data based on HNO_3 vapour pressure measurements, which covered the temperature range from 230 to 190 K. We adopt a parameterization of their data in our our table of preferred values in which:

$\log H^* = m / T - b$ where

$m = m_1[H_2SO_4]^2 + m_2[H_2SO_4] + m_3$ and $b = b_1[H_2SO_4]^2 + b_2[H_2SO_4] + b_3$

and the H_2SO_4 concentration $[H_2SO_4]$ is in wt.%

As pointed out by Taleb et al. (1996), at high temperature, Zhang's data are consistent with Vandoni's data. Taleb et al. also provide a more comprehensive model to predict vapour pressure and activity of H_2O, HNO_3 and H_2SO_4, which reproduces nicely the maximum in the HNO_3 vapor pressure of about 1:1 (mole fraction) $HNO_3 - H_2SO_4$ mixtures reported by Vandoni (1944) and which is in closer agreement with Zhang's data than the work of Luo et al. (1995).

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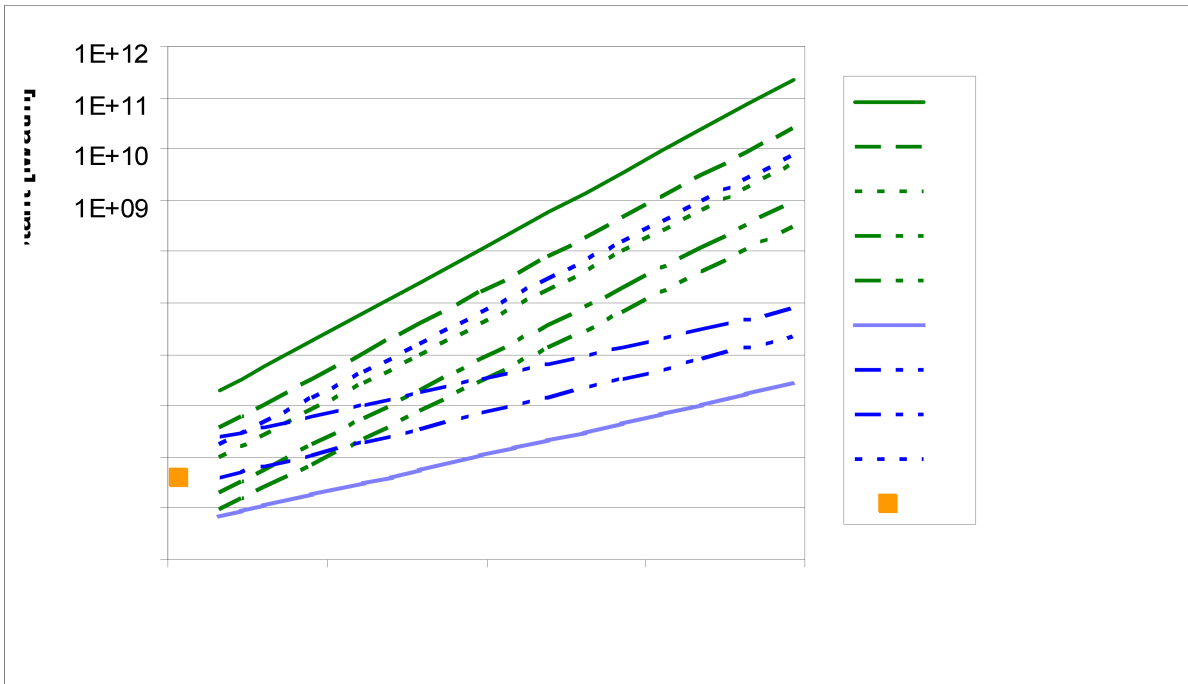Luo, B. P., Carslaw, K. S., Peter, T., and Clegg, S. L.: Geophys. Res. Lett., 22, 247-250, 1995.

Fig.1. Parameterization of effective solubility as a function of temperature. The lines are parameterizations used to fit experimental data. Green: Zhang et al. (2001) (recommended); blue: Reihs et al. (1990); the orange symbol represents the one data point reported by Van Doren et al. (1991).