IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.5 HET_SL_5

$$NO_2 + H_2SO_4 \rightarrow products$$
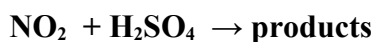
Experimental data

Parameter	[H_2SO_4] /wt %	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ				
$\gamma < 5.0 \times 10^{-6}$		193-243	Saastad et al., 1993	(a)
$(4.1\pm1.5) \times 10^{-7}$	45	298	Kleffmann et al., 1998	Bubbler-IC/IR (b)
$(2.5\pm0.5) \times 10^{-7}$	70			
$(5.2\pm0.5) \times 10^{-7}$	96			
$\gamma < 7.0 \times 10^{-7}$	39-68	203-243	Langenberg et al., 1998	(c)
Solubility: H				
0.5±0.1	39	243	Langenberg et al., 1998	(c)
1.4±0.5	59			
0.5±0.2	68			
50±7	39	203		
65±4	59			
37±6	68			
3.45×10^{-9} exp(4800/T)	59			
4.39×10^{-9} exp(4600/T)	68			

Comments

(a) Measurement of the total pressure drop in a static system over 70% H_2SO_4-H_2O monitored by MS. From its appearance, the solution was believed to be supercooled. NO_2 pressures were $10^{-5} – 10^{-2}$ mbar.

(b) NO_2 (10^{14} molecule cm^{-3}) in 740 Torr of N_2 was circulated through a thermostated bubbler containing 125 to 500 ml of water. NO_2 and HONO were measured using tunable diode laser absorption spectrometry. Nitrate and nitrite in the liquid was measured using ion chromatography, showing that they were initially formed at equimolar amounts. The first order rate constant for NO_2 decay did not depend on the NO_2 concentration, indicating overall first-order behaviour, and was proportional to the estimated bubble surface area. This led the authors to conclude that NO_2 uptake would be limited by a surface process. The increasing reactivity with increasing H_2SO_4 concentration was explained by formation of HNO_2^+ as intermediate.

(c) Measurement of chromatographic retention of NO_2 in a H_2SO_4 coated, thermostated quartz capillary using a chemiluminescence detector. Equilibrium with N_2O_4 was accounted for in the analysis. This experiment showed reactive loss of NO_2 of up to 40%.

Preferred Values

Parameter	Value	T/K
γ	$< 10^{-6}$ ($> 45\%$ H_2SO_4)	200 - 298
H	3.45×10^{-9} exp(4800/T) (59% H_2SO_4)	200 - 250
	4.39×10^{-9} exp(4600/T) (68% H_2SO_4)	
Reliability		
Δ log (γ)	undetermined	
Δ log (H)	0.5	200 - 250

Comments on Preferred Values

In view of the uncertainties related to the mass transfer characteristics pertinent to bubbler experiments (Lee and Schwartz, 1981; Cheung et al., 2000) it is not clear to what degree the experiment by Kleffmann et al. (1998) was solubility limited. Langenberg et al. (1998) provide an upper bound of the reactive uptake coefficient consistent with these values. We therefore used these to recommend an upper limit to the uptake coefficient and to extend the temperature range over that provided by Saastad et al. (1993).

No recommendation for the bulk accommodation coefficient is given. We adopt the temperature dependent solubility reported by Langenberg for the two higher acid concentrations. The temperature dependence corresponds to an enthalpy of solvation of -39.9 and – 38.5 kJ mol^{-1} for the 59 and 68 wt% solutions, respectively.

References

Cheung, J. L., Li, Y. Q., Boniface, J., Shi, Q., Davidovits, P., Worsnop, D. R., Jayne, J. T., and Kolb, C. E.: J. Phys. Chem. A, 104, 2655-2662, 2000.

Kleffmann, J., Becker, K. H., and Wiesen, P.: Atmos. Environ., 32, 2721-2729, 1998.

Lee, Y.-N., and Schwartz, S. E.: J. Phys. Chem., 85, 840-848, 1981.

Langenberg, S., Proksch, V., and Schurath, U.: Atmos. Environ., 32, 3129-3137, 1998.

Saastad, O. W., Ellermann, T., and Nielsen, C. J.: Geophys. Res. Lett., 20, 1191-1193, 1993.