

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.6 HET\_H2OL\_6

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hard copy without explicit written permission.

This data sheet first evaluated: May 2009.

## NH<sub>3</sub> + H<sub>2</sub>O (water droplets)

### Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: <math>\gamma, \gamma_{ss}, \gamma_0</math></i>			
0.040 <sup>+0.03</sup> <sub>-0.005</sub>	299	Bongartz <i>et al.</i> , 1995	LJ-IC (a)
0.097 ± 0.009	290	Ponche, George and Mirabel, 1993	DT-FTIR/HPLC (b)
0.1 (pH=0.5 - 3.0)	291	Shi <i>et al.</i> , 1999	DT-FTIR/MS (a)
0.06 (pH=8)	291		
0.006 (pH=10 - 13)	291		
0.35 (pH=0.5 - 3.0)	260		

### Comments

- (a) Uptake of NH<sub>3</sub> in a liquid jet of dilute HCl solution with continuous measurement of NH<sub>4</sub><sup>+</sup> in the collected jet waters. Contact time of 0.1 ms to 0.8 ms virtually free of saturation effects in the liquid phase. The  $\gamma$  values for air (+He) as carrier gas agreed very well with those measured in He ( $\gamma = 3.5 \times 10^{-2}$  in air vs.  $4.0 \times 10^{-2}$  in He).
- (b) Gas interaction with monodisperse (70  $\mu\text{m}$  to 110  $\mu\text{m}$  diameter) droplet train propagating axially in a low pressure (46 mbar to 93 mbar) flow tube. Uptake determined by ion chromatographic analysis of collected aqueous phase was independent of pH in the range 4.2 to 11.5 but dependent on the contact time and pressure. The value listed in the table has been corrected for gas phase diffusion. The measured average uptake coefficient  $\gamma_{\text{obs}}$  was  $(2.4 \pm 1.0) \times 10^{-2}$  at 93 mbar N<sub>2</sub> and 290 K, obtained by extrapolation to zero interaction time.
- (b) Uptake experiment of gas phase NH<sub>3</sub> on train of droplets whose size was in the range 150-300  $\mu\text{m}$  entrained in a flowing mixture of helium and water vapour (between 2.9 and 23.3 mbar). The reaction time was between 2 and 15 ms, the ammonia concentration was in the range  $10^{13}$  to  $2 \times 10^{14} \text{ cm}^{-3}$  and was monitored using a VUV lamp emitting at  $\lambda = 121.6 \text{ nm}$ . The theoretical framework included gas phase diffusion of ammonia, mass accommodation, dissolution, bulk and surface reaction whose relative contributions changed with pH. The effective Henry's law solubility was measured in the range 264 to 350 K:  $\log(H) = -3.221 + 1396/T$ . The uptake coefficient was dependent on pH, falling rapidly from  $\sim 0.08$  at pH=7 to 0.006 at pH=10. At low pH there is a negative temperature dependence of  $\gamma$ , which is attributed to accommodation controlled uptake. At high pH, NH<sub>3</sub> is less soluble and uptake controlled by a surface complex is suggested. Co-deposition with SO<sub>2</sub> enhanced the ammonia uptake to values corresponding to acidic solutions.

### Preferred Values

Parameter	Value	T/K
$\alpha$	0.1	290
$\alpha$	0.1	260 -300
	<i>Reliability</i>	
$\Delta \log (\gamma)$	$\pm 0.3$	290

#### *Comments on Preferred Values*

The uptake coefficients on pure water, measured using the droplet train technique are somewhat larger than onto dilute HCl in a liquid jet. Both methods require correction for gas phase diffusion and for saturation effects. On balance the DT experiment gives more reliable data we base the recommendation of the results of Ponche et al.(1993) and Shi et al., 1999), who also determined the temperature dependence at pH = 1. The value is higher than usually observed for the mass accommodation coefficient,  $\alpha_B$ , for uptake on pure water, and the strong dependence of  $\gamma$  on pH (Shi et al., 1999), indicates a direct chemical interaction of NH<sub>3</sub> at the surface, e.g. by protonation.

#### **References**

- Bongartz, A., Schweighofer, S., Roose, C. and Schurath, U.: J. Atmos. Chem. 20, 35 (1995).  
 Ponche, J.L., George, Ch. and Mirabel, Ph.: J. Atmos. Chem. 16, 1 (1993).  
 Shi, Q., Davidovits, P., Jayne, J.T., Worsnop, D.R. and Kolb, C.E.: J. Phys. Chem. A 103, 8812 (1999).