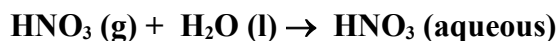


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.8 HET_H2OL_8

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Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>			
0.19±0.02	268	Van Doren et al., 1990	DT-IR (a)
0.071±0.02	293		
> 0.01	298	Kirchner et al., 1990	LJ-IC (b)
0.11±0.01	298	Ponche et al., 1993	DT-IC (c)
0.03	298	Schütze and Herrmann, 2002	(d)

Comments

- (a) Experiments performed at room temperature flow with the water vapor pressure adjusted to the vapour pressure of water at the experimental temperature. HNO₃ was detected downstream of the flow tube using IR absorption. The uptake coefficients were corrected for gas phase diffusion. The data show significant negative temperature dependence within the range indicated in the table. Given that under the experimental conditions the near surface region of the droplet does not saturate, it is argued that the uptake coefficients derived are actually bulk accommodation coefficients equivalent to the rate limiting step being solvation.
- (b) Interaction of HNO₃ (60 ppm) in 1 bar of synthetic air with a liquid jet of pure water. The kinetics were studied by ion chromatographic analysis of the liquid jet nitrate content. The uptake coefficient was attributed to a bulk accommodation coefficient and is regarded as a lower limit due to uncertainties in the velocity distribution of the liquid jet. The gas phase diffusion coefficient value used was 0.132 cm² s⁻¹, the value used for the effective solubility of HNO₃ in water was 2.45 × 10⁶ M² atm⁻¹.
- (c) Gas uptake into a monodisperse (70 μm to 110 μm diameter) droplet train. The pH of water was adjusted to 9.5 and 11.0. Uptake determined by chemical analysis (ion chromatography) of collected aqueous phase. The uptake coefficient corrected for gas phase diffusion was independent of pH, of the contact time and of the HNO₃ concentration in the range 10 to 100 ppm. The value for the diffusion coefficient used was 0.160 cm² s⁻¹ in the gas phase and 2.6 × 10⁻⁵ cm² s⁻¹ in the liquid phase. The solubility was assumed to be 2.1 × 10⁵ M atm⁻¹. The measured average uptake coefficient γ_{obs} was (5.0 ± 0.9) × 10⁻² at 67 mbar N₂ and 298 K.
- (d) A drop of water (2-3mm diameter) was exposed to HNO₃ (3-5 × 10¹³ cm⁻³) in a flow tube. The drop was probed by UV spectroscopy to monitor the appearance of nitrate in the aqueous phase. A model was used to determine the effect of gas phase diffusion on the measured uptake coefficient. The value for the gas phase diffusion coefficient was 0.124 cm² s⁻¹ in H₂O at 298 K and 0.534 atm cm² s⁻¹ in He at 298. The value used for the effective solubility of HNO₃ in water was 2.1 × 10⁵ M atm⁻¹. The measurements indicate that the uptake coefficient given in the table is a lower limit.

Preferred Values

Parameter	Value	T/K
α_b	$7.5 \times 10^{-5} \exp(2100/T)$	268 - 300
<i>Reliability</i>		
$\Delta \log(\alpha_b)$	0.7	
$\Delta E/R$ [K]	1000	

Comments on Preferred Values

The experiments on HNO₃ uptake to pure water all resulted in large uptake coefficients, and all studies concluded that bulk accommodation rather than solubility or reaction in the liquid phase (dissociation) was rate limiting. They all carry a significant uncertainty due to gas phase diffusion, depending on geometry and pressure. The high pressure liquid jet experiment by Kirchner et al. (1990) was most sensitively affected by the magnitude of the diffusion coefficient and in addition contained an uncertainty with respect to the liquid flow regime. Schütze and Herrmann (2002) also used several simplifications and suggest that their uptake coefficient represents a lower limit to the bulk accommodation coefficient. Also, the diffusion correction commonly applied for high uptake coefficients to the droplet train experiments as reported by Van Doren et al. (1990) has recently been challenged (Morita et al. 2003; Hanson et al., 2004; Garrett et al., 2006; Davidovits et al., 2006). Van Doren's experiments at high temperature were measured at higher total pressure than those at lower temperature. The two droplet train studies, in spite of determining uptake via loss of gas phase HNO₃ in one case (Van Doren et al., 1990) and the appearance of nitrate in the aqueous phase in the other (Ponche et al., 1993), but both using the same method to correct for diffusion, agree fairly well with each other. The recommended expression for α_b is a least square fit to the data by Ponche et al. and Van Doren et al. in Arrhenius form, with large error limits to account for potential systematic errors.

References

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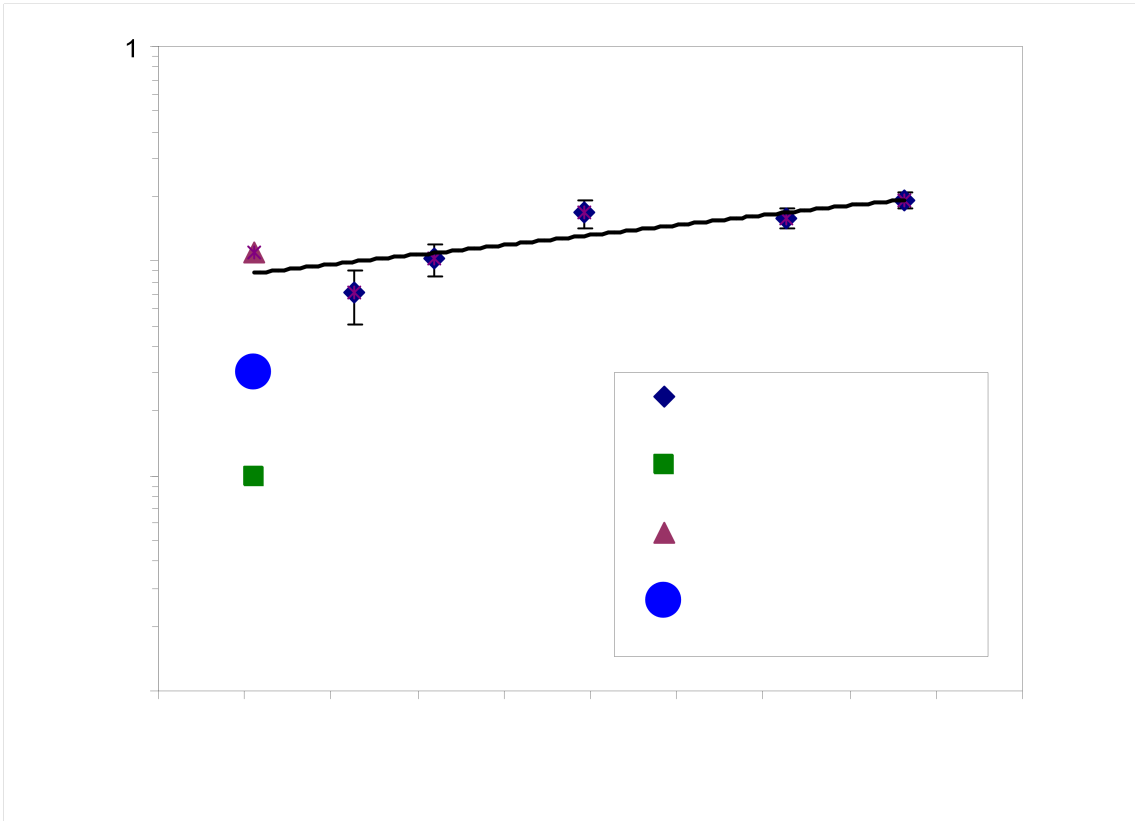


Figure 1: Uptake coefficients of HNO_3 into water as a function of temperature. Symbols denote data, the solid lines represents the recommended parameterisation for the bulk accommodation coefficient.