

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A4.09 HSTD9

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HNO₃ + SAT

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Experimental uptake coefficients: γ, γ_0</i>			
$\gamma_0 > 0.3$	191.5	Hanson, 1992	CWFT-CIMS a)
$\gamma_0 > 0.2$	200		
$\gamma_0 = 0.20$ 10% H ₂ SO ₄	180	Aguzzi and Rossi, 1991	Knud (b)
$\gamma_0 = 0.05$ 98% H ₂ SO ₄	180		
$\gamma_0 = 0.10$ 10% H ₂ SO ₄	200		
$\gamma_0 = 0.03$ 98% H ₂ SO ₄	200		
<i>Partition coefficients: $K(cm)$</i>			
No reversible adsorption observed			

Comments

- (a) HNO₃ uptake on SAT film made by freezing aqueous sulphuric acid solutions of composition 57.5 or 59.6 wt.% on the flow tube wall at <200 K. γ corrected for gas diffusion using estimated diffusion coefficients. Pressure = 0.6 mbar He. Rapid uptake observed, but with increasing surface coverage of HNO₃ the rate of uptake decreased. The steady-state partial pressure of HNO₃ over SAT surface at 191 K with a coverage of approximately 1 monolayer of HNO₃ was about a factor of ~3 higher than the vapor pressure over NAT, showing that new hydrate was not formed. At 200 K $p(\text{HNO}_3)$ was ~3x lower than over pure NAT. This is attributed to the formation of metastable NAM at this temperature.
- (b) SAT film made by freezing aqueous sulphuric acid solutions of composition indicated in wt.%. Uptake was continuous and γ was time independent except at the highest [H₂SO₄], when some decline with exposure time was noticed. The initial uptake coefficient decreased linearly with increasing [H₂SO₄] in the range given at both temperatures. If H₂O vapour was added to the flow into the Knudsen cell, the uptake coefficient was independent of [H₂SO₄] up to ~ 60-70%, depending on temperature.

Preferred Values

Parameter	Value	T/K
α_s	>0.2	190 – 240

Comments on Preferred Values

The results of the two experimental studies of nitric acid interaction with specifically prepared solid H₂SO₄-hydrate surfaces at temperatures and concentrations relevant for the lower stratosphere are in good agreement. Under these conditions uptake is rapid, continuous and irreversible, but declined with increasing coverage of surface HNO₃. Evidence from measurements of the p(HNO₃) over the surfaces indicated that the NAT-type solids formed on the surfaces were not in complete vapour-solid equilibrium. The data do not allow determination of the partition coefficient for adsorption, but the agreement between the results from different techniques allows us to recommended accommodation coefficient .

References

- Aguzzi, A. and Rossi, M.J.: Phys. Chem. Chem. Phys. 3, 3707 (2001).
Hanson, D. R.: J. Geophys. Res. Lett. 19, 2063 (1992).