The Kinetics of the Uptake of HNO_3 on Ice, Solid H_2SO_4/H_2O and Solid Ternary Solutions of $H_2SO_4/HNO_3/H_2O$ in the Temperature Range 180-211 K

Arnaud Aguzzi and Michel J. Rossi

Electronic Supplementary Information

Table E.1: Uptake coefficient of HNO_3 at T = 180 K.

Ice [(a)]	Flow [molec. s^{-1}]	Dose [molec.]	Concentration [molec. cm^{-3}]	k_{esc} [s^{-1}]	k_{uni} [s^{-1}]	γ_{obs}	γ_{corr} [(b)]
			PV experiments				
B		$2.8 \cdot 10^{12}$	$1.4 \cdot 10^{9}$	5.1	16.8	0.24	
B		$3.6 \cdot 10^{12}$	$1.8 \cdot 10^{9}$	4.8	22.4	0.32	
B		$5.9 \cdot 10^{12}$	$3.0 \cdot 10^{9}$	5.1	18.9	0.27	
B		$1.0 \cdot 10^{13}$	$5.0 \cdot 10^{9}$	5.2	18.9	0.27	
B		$1.1 \cdot 10^{13}$	$5.5 \cdot 10^{9}$	4.9	15.4	0.22	
B		$1.6 \cdot 10^{13}$	$8.0 \cdot 10^{9}$	4.6	21.7	0.31	
B		$1.9 \cdot 10^{13}$	$9.5 \cdot 10^{9}$	4.9	20.3	0.29	
B		$2.2 \cdot 10^{13}$	$1.1 \cdot 10^{10}$	4.3	19.6	0.28	
B		$3.5 \cdot 10^{13}$	$1.8 \cdot 10^{10}$	4.3	19.6	0.28	
B		$4.5 \cdot 10^{13}$	$2.3 \cdot 10^{10}$	4.2	18.2	0.26	
B		$1.0 \cdot 10^{14}$	$5.0 \cdot 10^{10}$	4.0	20.3	0.29	
			SS experiments				
C	$9.9 \cdot 10^{12}$		$2.1 \cdot 10^{9}$	2.4	14.0	0.20	0.27
B	$7.6 \cdot 10^{12}$		$2.7 \cdot 10^{9}$	1.4	16.1	0.23	0.28
B	$1.5 \cdot 10^{13}$		$3.7 \cdot 10^{9}$	2.0	18.9	0.27	0.32
C	$1.6 \cdot 10^{13}$		$4.4 \cdot 10^{9}$	1.8	16.8	0.24	0.29
B	$3.1 \cdot 10^{13}$		$6.5 \cdot 10^{9}$	2.4	20.3	0.29	0.31
B	$2.3 \cdot 10^{13}$		$6.7 \cdot 10^{9}$	1.7	16.1	0.23	-
B	$3.4 \cdot 10^{13}$		$7.0 \cdot 10^{9}$	2.4	20.3	0.29	-
B	$1.6 \cdot 10^{14}$		$4.0 \cdot 10^{10}$	2.0	20.3	0.29	0.30
C	$1.7 \cdot 10^{14}$		$4.4 \cdot 10^{10}$	2.0	18.9	0.27	0.31
C [(c)]	$1.1 \cdot 10^{14}$		$4.6 \cdot 10^{10}$	1.2	18.9	0.27	0.32
C	$5.0 \cdot 10^{15}$		$1.0 \cdot 10^{12}$	2.4	20.3	0.29	-
C	$5.1 \cdot 10^{15}$		$1.1 \cdot 10^{12}$	2.3	21.7	0.31	-

[(a)] Symbols are explained in the text.
[(b)] The corrected uptake coefficient has been obtained using equation (9).
[(c)] Experiments performed using the 8 mm aperture reactor.

Table E.2: Uptake coefficient of HNO_3 at T = 190 K.

Ice [(a)]	Flow [molec. s^{-1}]	Dose [molec.]	Concentration [molec. cm^{-3}]	k_{esc} [s^{-1}]	k_{uni} [s^{-1}]	γ_{obs}	γ_{corr} [(b)]
			PV experiments				
B		$3.1 \cdot 10^{12}$	$1.6 \cdot 10^{9}$	5.9	18.9	0.27	
B		$1.3 \cdot 10^{13}$	$6.5 \cdot 10^{9}$	5.5	17.5	0.25	
B		$1.6 \cdot 10^{13}$	$8.0 \cdot 10^{9}$	5.0	17.5	0.25	
			SS experiments				
B	$9.5 \cdot 10^{12}$		$2.3 \cdot 10^{9}$	2.1	18.9	0.27	-
B	$9.4 \cdot 10^{12}$		$2.6 \cdot 10^{9}$	1.8	16.1	0.23	0.27
C	$1.0 \cdot 10^{14}$		$3.1 \cdot 10^{10}$	1.6	18.2	0.26	0.30
B	$1.5 \cdot 10^{14}$		$3.3 \cdot 10^{10}$	2.2	14.0	0.20	0.21
C	$4.9 \cdot 10^{14}$		$1.1 \cdot 10^{11}$	2.2	18.9	0.27	-
C	$5.3 \cdot 10^{15}$		$1.3 \cdot 10^{12}$	2.1	16.8	0.25	-

(a) Symbols are explained in the text.

(b) The corrected uptake coefficient has been obtained using equation (9).

Table E.3: Uptake coefficient of HNO_3 at T = 200 K.

Ice [a]	Flow [molec. s^{-1}]	Dose [molec.]	Concentration [molec. cm^{-3}]	k_{esc} [s^{-1}]	k_{uni} [s^{-1}]	γ_{obs}	γ_{corr} [b]
			PV experiments				
B		$3.3 \cdot 10^{12}$	$1.7 \cdot 10^{9}$	5.5	11.9	0.17	
B		$6.2 \cdot 10^{12}$	$3.1 \cdot 10^{9}$	4.4	13.3	0.19	
B		$8.6 \cdot 10^{12}$	$4.3 \cdot 10^{9}$	5.6	11.9	0.17	
B		$1.3 \cdot 10^{13}$	$6.5 \cdot 10^{9}$	4.3	14.0	0.20	
B		$2.6 \cdot 10^{13}$	$1.3 \cdot 10^{10}$	4.4	12.6	0.18	
B		$3.7 \cdot 10^{13}$	$1.9 \cdot 10^{10}$	4.4	14.7	0.21	
B		$3.8 \cdot 10^{13}$	$1.9 \cdot 10^{10}$	4.0	12.6	0.18	
B		$1.0 \cdot 10^{14}$	$5.0 \cdot 10^{10}$	4.0	13.3	0.19	
			SS experiments				
B	$8.0 \cdot 10^{12}$		$1.6 \cdot 10^{9}$	2.5	10.5	0.15	0.18
C	$1.1 \cdot 10^{13}$		$1.8 \cdot 10^{9}$	3.0	11.9	0.17	-
B	$8.8 \cdot 10^{12}$		$1.8 \cdot 10^{9}$	2.5	10.5	0.15	0.20
C	$2.0 \cdot 10^{13}$		$3.7 \cdot 10^{9}$	2.7	10.5	0.15	0.16
B	$1.7 \cdot 10^{13}$		$4.3 \cdot 10^{9}$	2.0	12.6	0.18	0.23
B	$3.4 \cdot 10^{13}$		$1.1 \cdot 10^{10}$	1.6	12.6	0.18	0.23
B	$3.0 \cdot 10^{13}$		$1.2 \cdot 10^{10}$	1.3	9.8	0.14	0.15
C	$5.3 \cdot 10^{13}$		$1.2 \cdot 10^{10}$	2.2	11.9	0.17	-
B	$3.8 \cdot 10^{13}$		$1.4 \cdot 10^{10}$	1.4	10.5	0.15	0.18
B	$1.2 \cdot 10^{14}$		$2.3 \cdot 10^{10}$	2.2	11.2	0.16	0.16
B [c]	$8.7 \cdot 10^{14}$		$3.4 \cdot 10^{10}$	1.3	11.9	0.17	-
C	$1.1 \cdot 10^{14}$		$3.8 \cdot 10^{10}$	1.4	11.2	0.16	0.17
B	$1.9 \cdot 10^{14}$		$4.3 \cdot 10^{10}$	2.2	14.0	0.20	-
C [c]	$1.3 \cdot 10^{15}$		$5.9 \cdot 10^{11}$	1.1	9.8	0.15	-
C	$3.9 \cdot 10^{15}$		$9.3 \cdot 10^{11}$	2.1	11.2	0.16	-
C	$4.8 \cdot 10^{15}$		$1.2 \cdot 10^{12}$	2.0	12.6	0.18	-
C	$5.6 \cdot 10^{15}$		$1.8 \cdot 10^{12}$	1.6	13.3	0.19	-
C [c]	$8.3 \cdot 10^{15}$		$4.6 \cdot 10^{12}$	0.9	11.2	0.16	-

[a] Symbols are explained in the text.
[b] The corrected uptake coefficient has been obtained using equation (9).
[c] Experiments performed using the 8 mm aperture reactor.

Table E.4: Uptake coefficient of HNO_3 at T = 210 K.

Ice [(a)]	Flow [molec. s^{-1}]	Dose [molec.]	Concentration [molec. cm^{-3}]	k_{esc} [s^{-1}]	k_{uni} [s^{-1}]	γ_{obs}	γ_{corr} [(b)]
			PV experiments				
B		$4.7 \cdot 10^{12}$	$2.4 \cdot 10^{9}$	5.6	5.6	0.08	
B		$1.0 \cdot 10^{13}$	$5.0 \cdot 10^{9}$	5.7	5.6	0.08	
B		$2.9 \cdot 10^{13}$	$1.5 \cdot 10^{10}$	4.7	7.7	0.11	
B		$7.6 \cdot 10^{13}$	$3.8 \cdot 10^{10}$	4.2	7.0	0.10	
			SS experiments				
B	$1.8 \cdot 10^{13}$		$3.6 \cdot 10^{9}$	2.5	4.9	0.07	0.08
B	$2.5 \cdot 10^{13}$		$5.2 \cdot 10^{9}$	2.4	3.5	0.05	0.06
B	$9.8 \cdot 10^{13}$		$2.0 \cdot 10^{10}$	2.4	4.8	0.07	-

(a) Symbols are explained in the text.
(b) The corrected uptake coefficient has been obtained using equation (9).

Table E.5: Uptake coefficient of HNO_3 at T = 211 K.

Ice [(a)]	Flow [molec. s^{-1}]	Concentration [molec. cm^{-3}]	k_{esc} [s^{-1}]	k_{uni} [s^{-1}]	γ_{obs}	γ_{corr} [(b)]
B	$9.4 \cdot 10^{12}$	$3.6 \cdot 10^{9}$	1.3	5.6	0.08	0.09
C	$1.5 \cdot 10^{14}$	$2.9 \cdot 10^{10}$	2.5	4.2	0.06 [(c)]	-
C	$2.1 \cdot 10^{14}$	$4.4 \cdot 10^{10}$	2.4	3.5	0.05 [(c)]	-

(a) Symbols are explained in the text.
(b) The corrected uptake coefficient has been obtained using equation (9).
(c) Partial saturation of the ice sample has been observed.

Table E.6: Mean composition of the $HNO_3 \cdot nH_2O$ condensed phase. Experiments performed on condensed ice samples.

T [K]	γ	C [(a)] [molecules]	h [(b)] [nm]	HNO_3(cond) [molecules]	n	t [(c)] [s]	P(HNO_3) [Torr]	P(H_2O) [Torr]
180	0.29	$4.50 \cdot 10^{18}$	100	$9.01 \cdot 10^{17}$	4.1 [(d)]	160	$1.6 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$
180	0.29	$4.50 \cdot 10^{18}$	100	$1.21 \cdot 10^{18}$	3.0 [(e)]	560	$2.4 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$
180	0.31	$4.65 \cdot 10^{19}$	1100	$8.80 \cdot 10^{17}$	4.5 [(f)]	185	$1.6 \cdot 10^{-5}$	$8.7 \cdot 10^{-5}$
180	0.31	$4.65 \cdot 10^{19}$	1100	$1.34 \cdot 10^{18}$	2.8 [(f)]	530	$3.4 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$
190	0.25	$2.78 \cdot 10^{18}$	65	$6.31 \cdot 10^{17}$	1.2	145	$4.1 \cdot 10^{-5}$	$2.5 \cdot 10^{-6}$
190	0.27	$9.01 \cdot 10^{19}$	2120	$1.12 \cdot 10^{18}$	1.1	2450	$3.3 \cdot 10^{-4}$	$4.5 \cdot 10^{-5}$
200	0.18	$1.19 \cdot 10^{19}$	280	$4.39 \cdot 10^{17}$	1.8	120	$3.5 \cdot 10^{-5}$	$1.9 \cdot 10^{-6}$
200 [(g)]	0.16	$1.42 \cdot 10^{19}$	330	$1.64 \cdot 10^{18}$	1.2	230	$6.0 \cdot 10^{-5}$	$9.7 \cdot 10^{-6}$
200 [(g)]	0.15	$2.87 \cdot 10^{19}$	670	$5.85 \cdot 10^{17}$	0.9	495	$1.0 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$
200	0.16	$3.89 \cdot 10^{19}$	916	$1.47 \cdot 10^{18}$	1.1	401	$8.0 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$
200	0.19	$1.11 \cdot 10^{20}$	2610	$4.01 \cdot 10^{18}$	1.1	740	$3.0 \cdot 10^{-5}$	$1.9 \cdot 10^{-6}$

[(a)] Number of H_2O molecules condensed on the cold support.
[(b)] Thickness of the condensed ice sample ($\rho = 0.92$ gr cm^{-3}).
[(c)] Time at which the phase transition has been observed after the opening of the sample compartment.
[(d)] Value measured at t = 220 s in **Figure 5.a**.
[(e)] Value measured at t = 620 s in **Figure 5.a**.
[(f)] Same type of experiment as displayed in **Figure 5.a**.
[(g)] Experiments performed using the 8 mm aperture reactor.

Table E.7: Quantity of HNO_3 in ML adsorbed on the condensed ice sample, mean distance d of penetration of HNO_3 into the bulk and thickness h of the condensate.

T [K]	Adsorbed HNO_3/ML	d [(a)] [nm]	h [nm]
180	16 [(b)]/106 [(c)]	3.7 [(b)]/8.6 [(c)]	102 [(b)]/87 [(c)]
180	20/104	3.9/9.0	741/94
190	14/74	8.7/19.1	56/22
190	10/132	12.0/24.8	2052/28
200	15/52	15.6/39.8	219/35
200	35/193	22.4/54.0	252/45
200	16/69	44.1/78.4	346/85
200	24/173	33.3/70.3	257/50
200	35/472	41.3/97.0	1976/101

[(a)] $d = \sqrt{Dt}$, where $D = 1.37 \cdot 10^{-2610/T}$ [Thibert, 1998].
[(b)] Measured when H_2O partial pressure begins to decrease.
[(c)] Measured at the phase transition.

Table E.8: Uptake coefficient of HNO_3 on solid ternary solutions of $H_2SO_4/HNO_3/H_2O$.

T [K]	H_2SO_4 [(a)] [wt %]	HNO_3 [(a)] [wt %]	Flow [molecule s^{-1}]	k_{esc} [s^{-1}]	γ_{obs} [(b)]
185	1	20	$4.3 \cdot 10^{14}$	1.6	0.11
185	1	20	$5.4 \cdot 10^{14}$	1.6	0.11
185	1	20	$7.7 \cdot 10^{14}$	1.4	0.12
190	5	40	$9.5 \cdot 10^{13}$	2.2	0.08
190	5	40	$2.3 \cdot 10^{14}$	2.1	0.12
192	20	20	$5.4 \cdot 10^{14}$	1.9	0.12
192	20	20	$7.4 \cdot 10^{14}$	1.7	0.10
195	50	1	$3.4 \cdot 10^{14}$	1.9	0.09
195	50	1	$6.0 \cdot 10^{14}$	2.1	0.08

(a) STS compositions from Carslaw *et al.* [1994].
(b) No correction has been applied on γ values due to large HNO_3 flow rates used in these experiments (see Part D for details).