ADDITIONS AND CORRECTIONS

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Benoît Flückiger, Laurent Chaix, and Michel J. Rossi*: Properties of the HCl/Ice, HBr/Ice, and H_2O/Ice Interface at Stratospheric Temperatures (200 K) and Its Importance for Atmospheric Heterogeneous Reactions

Pages 11739−11750. Equations 6 and 7 of the above-mentioned publication contain a regrettable error in that R_{evap}, the rate of evaporation of H_2O from ice, has been confused with the NET rate of evaporation $F_0 = R_{evap} - R_{cond}$ which should have been used in the first place. The rate of condensation of water vapor, R_{cond}, on the ice substrate may not be neglected in the used low-pressure flow reactor in the temperature range of interest. The correct equations describing the loss of H_2O from the ice sample owing to hydrolysis of $ClONO_2$, reaction R-2, and evaporation are therefore

$$-\frac{dN(H_2O)}{dt} = k_2[ClONO_2]V + F_0 \tag{6}$$

where $F_0 = k_{esc}$ $[H_2O]V$ is the rate of effusion of water vapor at steady-state conditions giving rise to a MS signal at m/e 18 for H_2O and

$$h = (k_2[ClONO_2]V + F_0)\left(\frac{k_1}{k_2}\right)t_1\frac{d}{1.6 \times 10^{16}} \tag{7}$$

Because F_0 has not been measured in these experiments by recording the calibrated MS signal at m/e 18, it was calculated from the data of Chaix et al.[11] using eq 7a for $T = 190$ and 200 K:

$$F_0 = (P_{H_2O}/RT)V(k_c k_{esc}/k_c + k_{esc}) \tag{7a}$$

where P_{H_2O}, k_c and k_{esc} are the partial pressure of H_2O (2.42×10^{-4} Torr at 190 K and 1.22×10^{-3} Torr at 200 K) over ice, the condensation (21 s^{-1} at 190 K and 18 s^{-1} at 200 K) and escape rate constants (6.6 s^{-1}), respectively. Table 5 displays the thickness of the interface h calculated according to eq 7 for the different ice samples. Table 6 presents the average values of h for the three types of ice examined in this work and the recalculated diffusion coefficients of HCl in ice, D_{HCl}, as a function of the average interface thickness h. Although the numerical values of h are now significantly smaller than in the original publication amounting to approximately one-third of the value of the published ones, the main conclusion of the study remains unchanged. It may be summarized by stating that HCl is distributed over a layer tens of nm thick in an open interfacial structure whose HCl content rapidly interacts with the gas-phase such as reaction R-1. The resulting diffusion coefficients D_{HCl} for the HCl/ice interface have decreased as a consequence of the increased average mole fraction X_{HCl} within the interface thickness h. A forthcoming publication[51] will present a synopsis of the measured diffusion coefficients of HCl and HBr in ice obtained by using the DPE ("dope and probe") technique presented in this work. In this more recent study,[51] F_0 has been measured for every experiment such that the estimate according to eq 7a may be replaced with experimental data obtained under identical conditions to those of the measurement of the rate of halogen exchange, reaction R-1, and hydrolysis of chlorine nitrate, reaction R-2.

51. Aguzzi, A.; Flückiger, B.; Rossi, M. J. The Nature of the Interface and the Diffusion Coefficient of HCl/Ice and HBr/Ice in the Temperature Range 190−205 K. *Phys. Chem. Chem. Phys.* **2003**, Submitted.

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TABLE 5: Calculated Values of the Interfacial Thickness *I* and HCl Mole Fraction X_{HCl} in the Interface Region

ice	T [K]	$F^i(ClONO_2)$ [molecule s^{-1}]	$N(H_2O)$ [molecules]	N(HCl) [molecules]	total ice thickness H [μm]	t_1 [s]	t_{exp} [s]	h^a [nm]	$X_{HCl}{}^b$
C*	190	6×10^{15}	9.4×10^{19}	4×10^{15}	2.3	10	300	123	8×10^{-4}
C*	200	3.75×10^{15}	3.8×10^{19}	6.3×10^{15}	0.9	10	-	614	3×10^{-4}
C	190	3.8×10^{15}	1.5×10^{20}	2.5×10^{16}	3.8	7	660	86	7×10^{-3}
C	190	4.4×10^{15}	2.8×10^{20}	1.3×10^{16}	7.0	6	220	73	4×10^{-3}
C	190	4.8×10^{15}	3.3×10^{20}	1.9×10^{16}	8.2	5	1100	61	8×10^{-3}
C	190	5.2×10^{15}	5.5×10^{19}	1.3×10^{16}	1.3	7	240	86	4×10^{-3}
C	190	5.2×10^{15}	1.0×10^{20}	1.3×10^{16}	2.5	7	414	86	4×10^{-3}
C	190	6.5×10^{15}	1.6×10^{20}	1.2×10^{16}	4.1	3	1400	37	8×10^{-3}
B	190	4.8×10^{15}		1.6×10^{16}		11	-	135	3×10^{-3}
B	200	3.9×10^{15}		9.0×10^{15}		5	-	307	7×10^{-4}
SC	190	3.8×10^{15}		1.4×10^{16}		5	-	61	6×10^{-3}

[a] h is calculated according to eq 7. [b] X_{HCl} is the HCl mole fraction in the interface region of thickness h, calculated according to $X_{HCl} = (N(HCl)/h)(d/1.6 \times 10^{16})$, $d = 0.4$ nm is the thickness of one nominal layer of water ice and 1.6×10^{16} is the total number of surface molecules of H_2O for the sample (geometric) surface area of 15 cm^2.

TABLE 6: Diffusion Coefficient D_{HCl} as a Function of the Type of Ice, Calculated According to Fick's First Law and Fick's Second Law at $T = 190$ K

		D_{HCl} [cm^2 s^{-1}]		
ice	h [nm]	F_L [molecule s^{-1} cm^{-2}]	Fick's first law [a]	Fick's second law [b]
SC	60 ± 10	$(2 \pm 1) \times 10^{11}$	$(8.0 \pm 0.5) \times 10^{-15}$	$(4.0 \pm 0.5) \times 10^{-15}$
C	70 ± 20	$(7 \pm 3) \times 10^{11}$	$(3.9 \pm 0.5) \times 10^{-14}$	
B	130 ± 20	$(7 \pm 3) \times 10^{11}$	$(1.2 \pm 0.5) \times 10^{-13}$	$(0.6 \pm 0.5) \times 10^{-13}$

[a] Calculated according to eq 11. [b] Fitted values to data of Figure 10 according to eq 12.