Supplement to Heterogeneous Kinetics of H$_2$O, HNO$_3$ and HCl on HNO$_3$ hydrates (α-NAT, β-NAT, NAD) in the range 175-200 K

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Supplement A

Langmuir adsorption isotherms for H$_2$O, HNO$_3$ and HCl on stainless-steel reactor walls at 315 K

Figures

Figure S1: Wall coverage as a function of gas X concentration interacting with the reactor walls according to Langmuir adsorption. The dark and light blue symbols represent the interaction of pure H$_2$O and of H$_2$O in the presence of an additional HCl flow admitted into the reactor, respectively. Similarly, the red and orange symbols represent the interaction of pure HCl and of HCl in the presence of an additional H$_2$O flows admitted into the reactor. The dark and light green symbols represent the interaction of pure HNO$_3$ and of HNO$_3$ in the presence of an additional H$_2$O flow. The additional flows as well as parameters for the best fit curves are reported in Table 2 in the main text.
Supplement B

Thermodynamic Considerations for $\alpha$-NAT

A van t’Hoff plot of the corresponding vapor pressures $P_{eq}(H_2O)$ is displayed in Figure S2 and the best linear fit for two-orifice and PV measurements are reported in Eqs. (S1) and (S2):

\[
\log P_{eq}(H_2O) [\text{Torr}] = (15.2 \pm 4.0) - \frac{(70.3 \pm 14.1) \times 10^3}{2.303 \, RT} \quad \text{(S1)}
\]
\[
\log P_{eq}(H_2O) [\text{Torr}] = (11.8 \pm 1.5) - \frac{(56.5 \pm 5.1) \times 10^3}{2.303 \, RT} \quad \text{(S2)}
\]

The two temperature dependent regimes are not clearly evident in the vapor pressures, as the temperature dependences of $\alpha(H_2O)$ and $R_{ev}(H_2O)$ tend to compensate each other at low temperatures. For this reason, we may also calculate the best fit line for PV experiments excluding points at temperatures lower than 180 K. We display the results of the fit for this reduced dataset as the black dashed line in Figure S1.

We calculate the enthalpies of evaporation for two-orifice (TO) and PV experiments as $\Delta H_{ev,TO}^0(H_2O) = (70.3 \pm 14.1) \text{ kJ mol}^{-1}$ and $\Delta H_{ev,PV}^0(H_2O) = (56.5 \pm 5.1) \text{ kJ mol}^{-1}$, respectively. For comparison, the enthalpy of evaporation corresponding to the dashed black line is $\Delta H_{ev,TO}^0(H_2O) = (82.0 \pm 30.0) \text{ kJ mol}^{-1}$. The values calculated are the same within experimental uncertainty, and if we take the average value for the two measurements techniques of $\Delta H_{ev}^0(H_2O) = (63.4 \pm 9.6) \text{ kJ mol}^{-1}$ we estimate an activation energy of the accommodation process of H$_2$O on $\alpha$-NAT of $E_{acc}(H_2O) = E_{ev}(H_2O) - \Delta H_{ev}^0(H_2O) = (75.3 - 63.4) = (11.9 \pm 9.8) \text{ kJ mol}^{-1}$, a positive activation energy similar to the case of HCl hexahydrate, for which $E_{acc}(\text{HCl}) = (21.2 \pm 17.0) \text{ kJ mol}^{-1}$ (Iannarelli and Rossi, 2014). In analogy with the case of HCl•6H$_2$O, the positive activation energy may have to do with the high value of activation energy $E_{ev}(H_2O)$ out of the crystalline environment of $\alpha$-NAT.

Bibliography

Iannarelli, R. and Rossi, M. J.: H$_2$O and HCl trace gas kinetics on crystalline HCl hydrates and amorphous HCl/H$_2$O in the range 170 to 205 K: The HCl/H$_2$O phase diagram revisited, Atmos. Chem. Phys., 14(10), 5183-5204, 2014.
**Figure S2:** Summary van ‘t Hoff plot of $P_v(H_2O)$ for α-NAT. Full and empty red circles represent results of PV (Pulsed Valve) and TO (Two Orifice) experiments, respectively. The equations for the linear fits may be found in the text. The black dashed line represent the best fit of PV results above 180 K.
Supplement C

Pulsed Valve Experiments and Saturation

Figures

Figure S3: H$_2$O pulse series on α-NAT and β-NAT substrates. Red circles and black squares represent series of H$_2$O pulses on α- and β-NAT, respectively. The numbers label the first and second pulse of a series.
Supplement D

Summary van’t Hoff Plot for HNO$_3$ and adsorbed HCl on $\alpha$- and $\beta$-NAT

**Figure S4:** Summary of van t’Hoff plots of $P_{\text{ev}}$(HNO$_3$) and $P_{\text{ev}}$(HCl) for $\alpha$- and $\beta$-NAT, respectively. HNO$_3$ and HCl experiments correspond to TO and PV experiments, respectively. The equations for the linear fits may be found in the text.