Supplement to Heterogeneous Kinetics of H_2O, 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_2O, HNO_3 and HCl on stainless-steel reactor walls at 315 K

Figures

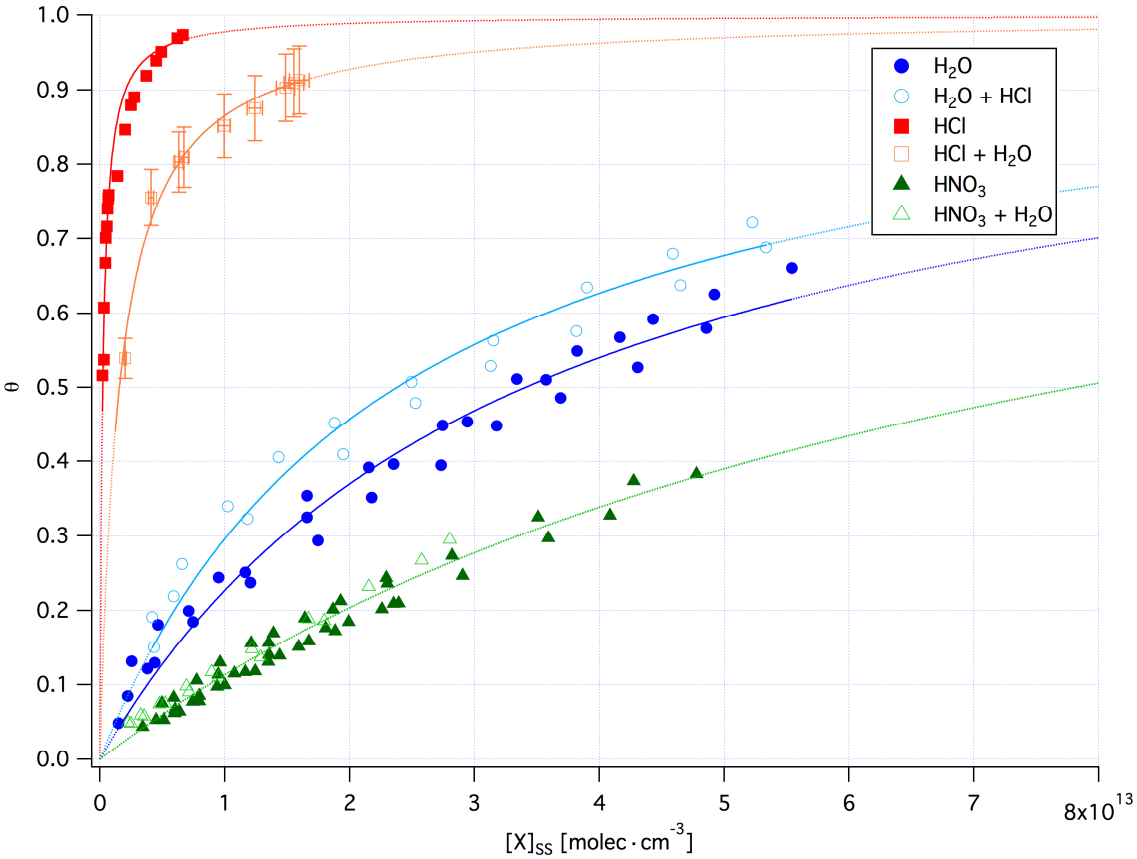

Figure S1: Wall coverage as a function of gas X concentration interacting with the reactor walls according to Langmuir adsorption. The dark and light blue symbols represent the interaction of pure H_2O and of H_2O in the presence of an additional HCl flow admitted into the reactor, respectively. Similarly, the red and orange symbols represent the interaction of pure HCl and of HCl in the presence of an additional H_2O 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_2O 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 α-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 $\Delta H^0_{ev,TO}(H_2O)$ = (70.3 ± 14.1) kJ mol^{-1} and $\Delta H^0_{ev,\,PV}(H_2O)$ = (56.5 ± 5.1) kJ mol^{-1}, respectively. For comparison, the enthalpy of evaporation corresponding to the dashed black line is $\Delta H^0_{ev,TO}(H_2O)$ = (82.0 ± 30.0) 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 $\Delta H^0_{ev}(H_2O)$ = (63.4 ± 9.6) kJ mol^{-1} we estimate an activation energy of the accommodation process of H_2O on α-NAT of $E_{acc}(H_2O) = E_{ev}(H_2O) - \Delta H^0_{ev}(H_2O)$ = (75.3 - 63.4) = (11.9 ± 9.8) kJ mol^{-1}, a positive activation energy similar to the case of HCl hexahydrate, for which $E_{acc}(HCl)$ = (21.2 ± 17.0) kJ mol^{-1} (Iannarelli and Rossi, 2014). In analogy with the case of $HCl \bullet 6H_2O$, 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 α-NAT.

Bibliography

Iannarelli, R. and Rossi, M. J.: H_2O and HCl trace gas kinetics on crystalline HCl hydrates and amorphous HCl/H_2O in the range 170 to 205 K: The HCl/H_2O phase diagram revisited, Atmos. Chem. Phys., 14(10), 5183-5204, 2014.

Figures

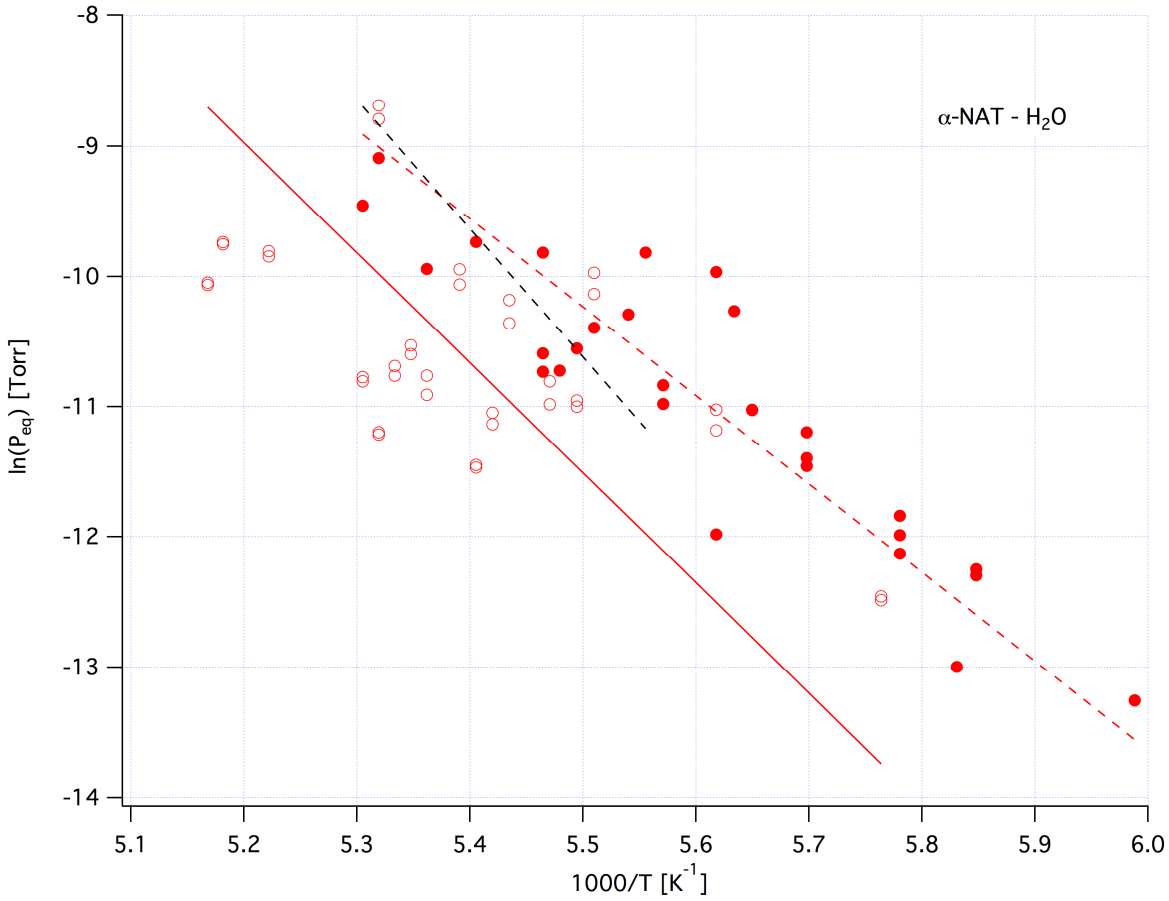

Figure S2: Summary van t'Hoff plot of $P_{ev}(H_2O)$ for α-NAT. Full and empty red circles represent results of PV (Pulsed Valve) and TO (Two Orifice) experiments, respectively. The equations for the linear fits may be found in the text. The black dashed line represent the best fit of PV results above 180 K.

Supplement C

Pulsed Valve Experiments and Saturation Figures

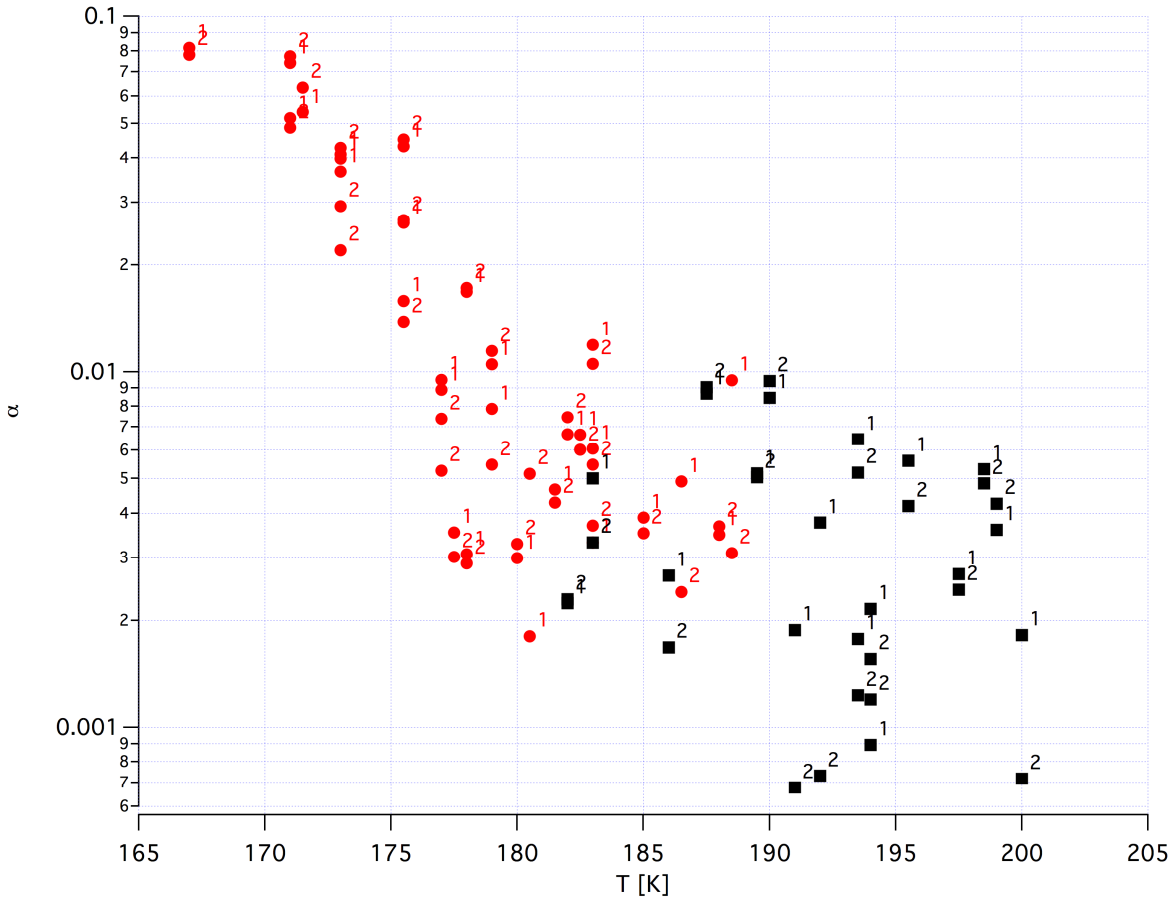

Figure S3: H_2O pulse series on α-NAT and β-NAT substrates. Red circles and black squares represent series of H_2O pulses on α- and β-NAT, respectively. The numbers label the first and second pulse of a series.

Supplement D

Summary van't Hoff Plot for HNO_3 and adsorbed HCl on α- and β-NAT

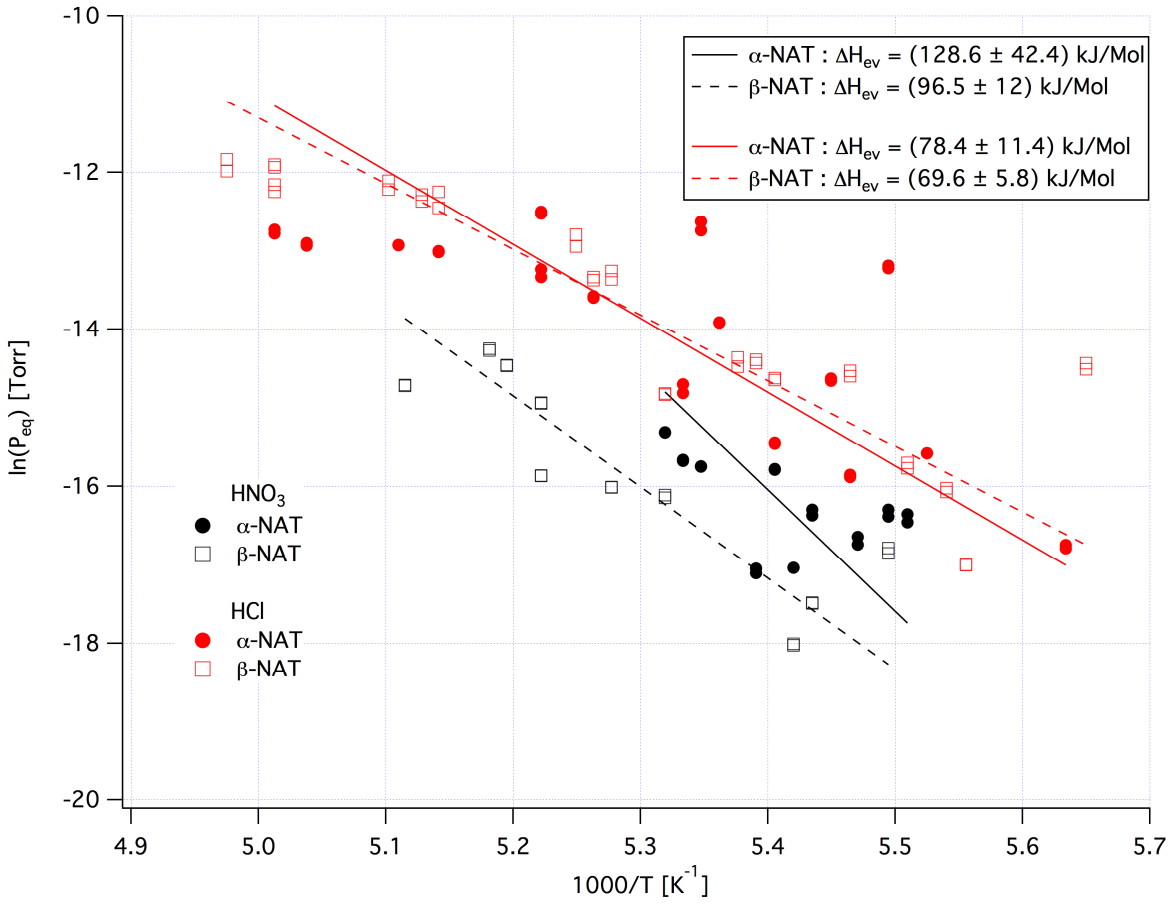

Figure S4: Summary of van t'Hoff plots of $P_{ev}(HNO_3)$ and $P_{ev}(HCl)$ for α- and β-NAT, respectively. HNO_3 and HCl experiments correspond to TO and PV experiments, respectively. The equations for the linear fits may be found in the text.