



Thermochemical Kinetics of H₂O and HNO₃ on crystalline Nitric Acid Hydrates (alpha-, beta-NAT, NAD) in the range 175-200 K

Michel J. Rossi and Riccardo Iannarelli

Paul Scherrer Institute (PSI), Labor f. Atmosphärenchemie, Villigen PSI, Switzerland (michel.rossi@psi.ch)

The growth of NAT (Nitric Acid Trihydrate, HNO₃·3H₂O) and NAD (Nitric Acid Dihydrate, HNO₃·2H₂O) on an ice substrate, the evaporative lifetime of NAT and NAD as well as the interconversion of alpha- and beta-NAT competing with evaporation and growth under UT/LS conditions depends on the interfacial kinetics of H₂O and HNO₃ vapor on the condensed phase. Despite the existence of some literature results we have embarked on a systematic investigation of the kinetics using a multidagnostic experimental approach enabled by the simultaneous observation of both the gas (residual gas mass spectrometry) as well as the condensed phase (FTIR absorption in transmission).

We report on thermochemically consistent mass accommodation coefficients alpha and absolute evaporation rates $R_{ev}/\text{molecule s}^{-1}\text{cm}^{-3}$ as a function of temperature which yields the corresponding vapor pressures of both H₂O and HNO₃ in equilibrium with the crystalline phases, hence the term thermochemical kinetics. These results have been obtained using a stirred flow reactor (SFR) using a macroscopic pure ice film of 1 micron or so thickness as a starting substrate mimicking atmospheric ice particles and are reported in a phase diagram specifically addressing UT (Upper Troposphere)/LS (Lower Stratosphere) conditions as far as temperature and partial pressures are concerned. The experiments have been performed either at steady-state flow conditions or in transient supersaturation using a pulsed solenoid valve in order to generate gas pulses whose decay were subsequently monitored in real time. Special attention has been given to the effect of the stainless-steel vessel walls in that Langmuir adsorption isotherms for H₂O and HNO₃ have been used to correct for wall-adsorption of both probe gases.

Typically, the accommodation coefficients of H₂O and HNO₃ are similar throughout the temperature range whereas the rates of evaporation R_{ev} of H₂O are significantly larger than for HNO₃ thus leading to the difference in vapor pressure revealed in the phase diagram. A noteworthy effect seems to be that the accommodation coefficients obtained in pulsed gas admission experiments (transient supersaturation) lead to significantly lower values owing to surface saturation, especially in the case of the thermodynamically stable beta-NAT substrate.