

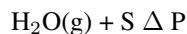


## The temperature- and pressure-dependent mass accommodation coefficient $\alpha$ of $\text{H}_2\text{O}$ vapor on atmospheric ices in the range 160 to 200 K

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Real-time uptake experiments of  $\text{H}_2^{16}\text{O}$  vapor on thin ice films based on pulsed valve admission of water vapor have been performed both in a Knudsen flow reactor as well as in a stirred-flow reactor in the range 160 to 200 K in the molecular flow regime. Mass-spectrometric detection of water vapor was used in both cases and the emphasis in the present work was placed on pure  $\text{H}_2^{16}\text{O}$  ice. In the aftermath of pulsed admission of  $\text{H}_2\text{O}$  vapor into the Knudsen flow reactor in the presence of an ice sample a first-order decay of the m/e 18 MS signal was observed, whereas for experiments performed in the stirred-flow reactor a more complex time-dependent MS signal was detected consisting of a rapid initial first-order decay followed by a slower decaying signal that depended on the admitted dose and the temperature of the ice and that was lingering on for several seconds. The dose was varied by a factor of approximately 200-500 with the lowest dose depending on the ice substrate temperature which was varied in the range 160 to 200 K. Two basic facts emerged from the experiments: (a) the mass accommodation coefficient  $\alpha$  determined from the initial fast-decaying portion of the MS signal decreased with temperature thus showing a negative activation energy; (b)  $\alpha$  significantly increased with the applied dose corresponding to an increase of  $\alpha$  by up to a factor of 30 when the dose was increased by a factor of 200. In addition to the previously discovered negative temperature dependence the uptake kinetics  $\alpha$  of water vapor is dependent on the instantaneous pressure or supersaturation ratio and may be represented by the following complex reaction mechanism of Flückiger et al. (2003) where  $\text{H}_2\text{O}$  interacts with a surface site S located on a water-ice substrate:



The new data confirm the common precursor state chemical kinetic model of Flückiger combining both the presence of a weakly-bound precursor P as well as the autocatalytic acceleration of the rate of the incorporation of additional water vapor  $\text{H}_2\text{O(g)}$  into bulk ice  $\text{H}_2\text{O(B)}$ . As a corollary, the results obtained from the study of  $\alpha$  using different laboratory experiments depend on the degree of supersaturation of  $\text{H}_2\text{O}$  vapor used to "interrogate" the ice surface. The present result may help to elucidate puzzling and controversial observations giving rise to recent scientific discussions in the atmospheric science literature. Two examples may be cited: Kulmala et al. and Wagner et al. measured  $\alpha = 1.0$  using cloud expansion chamber experiments coupled to constant-angle Mie scattering detection, whereas Kolb et al (Aerodyne) obtained a significantly lower  $\alpha$  value from the uptake of  $\text{H}_2\text{O}$  vapor onto small water droplets, typically  $\alpha = 0.15$ . These results may be reconciled when realizing that these two groups of experiments have been performed at significantly differing  $\text{H}_2\text{O}$  supersaturation ratios. Another group of experiments concerns field measurements of water vapor supersaturation ratios in the upper troposphere/lower stratosphere where supersaturation ratios of up to 130% have been found (Fahey and coworkers). The observed  $\text{H}_2\text{O}$  supersaturation could be related to the lingering transients observed in laboratory experiments after pulsed admission of  $\text{H}_2\text{O}$  water vapor. In addition to pure  $\text{H}_2\text{O}$  ice substrates preliminary data of  $\text{H}_2\text{O}$  uptake on  $\text{HCl}$  and  $\text{HNO}_3$ -doped ice substrates will briefly be presented, time permitting.