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Modeling the non-ideal chemical processing in aqueous aerosol particles with SPACCIM-SpactMod

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Highly-polluted urban regions are often characterized by high aerosol particle loadings impacting atmospheric chemistry and, hence, air quality. Tropospheric deliquesced particles including haze particles are a complex multiphase and multi-component environment with simultaneously occurring multiphase chemical transformations. Such chemical processes are able to alter the chemical composition and the deduced physical aerosol properties. Deliquesced particles are characterized by concentrated non-ideal solutions that can affect the occurring multiphase chemical processing. The effects of such non-ideal solutions have generally not been adequately investigated by present complex multiphase chemistry models. Thus, the present study is aimed at accessing the impact of non-ideality on multiphase chemical processing. Therefore, simulations with a multiphase chemistry model (SPACCIM-SpactMod) including the CAPRAM chemical mechanism are performed for polluted and less polluted environmental conditions. The present study shows that activity coefficients of inorganic ions are often below unity under deliquesced aerosol conditions, and that most uncharged organic compounds exhibit activity coefficient values around or even above unity. The model studies demonstrated that the inclusion of non-ideality considerably affects the multiphase chemical processing of transition metal ions (TMIs), key oxidants, and related chemical subsystems, e.g. organic chemistry.

In detail, both the chemical formation and oxidation fluxes of Fe(II) are substantially lowered by a factor of 2.8 under polluted haze conditions compared to a case study without non-ideality treatment. The reduced Fe(II) processing in the polluted base case, including lowered chemical fluxes of the Fenton reaction (-70 %), results in a reduced processing of HO_x/HO_y. under deliquesced aerosol conditions. Therefore, higher multiphase H_2O_2 concentrations (by a factor of 3.1 larger) and lower aqueous-phase OH concentrations (by a factor of ≈ 4 lower) were modeled during aerosol conditions. For H_2O_2, the consideration of non-ideality increases S(VI) oxidation fluxes under aqueous aerosol conditions by 40 %. Moreover, the chemical fluxes of the OH radical are about 50 % lower in the non-ideal haze case. Accordingly, the consideration of non-ideality affects the chemical processing and the concentrations of organic compounds under deliquesced particle conditions in a compound-specific manner. For important organic carboxylic acids, e.g. glyoxylic acid and oxalic acid, the reduced radical oxidation budget under aqueous particle conditions leads to increased concentration levels. For oxalic acid, the present study demonstrates that the non-ideality treatment enables more realistic predictions of high oxalate concentrations observed under ambient highly polluted conditions. Furthermore, the simulations show that lower humidity conditions, i.e. more concentrated solutions, might promote higher oxalic acid concentration levels in aqueous aerosols due to differently affected formation and degradation processes. Overall, the performed studies demonstrate the important role of a detailed non-ideality treatment in multiphase models dealing with aqueous aerosol chemistry and the needs to further improve current model implementations.