

Thermodynamics of carbonates and hydrates related to heterogeneous reactions involving mineral aerosol.

James T. Kelly^{1,4} and Anthony S. Wexler^{1,2,3}

Department of Mechanical and Aeronautical Engineering¹

Department of Civil and Environmental Engineering²

Department of Land, Air and Water Resources³

University of California, Davis

Atmospheric Science Division⁴

Lawrence Livermore National Laboratory, Livermore, CA

Large amounts of mineral aerosol are emitted from arid regions of the earth and are transported widely around the globe. Carbonates in mineral aerosol may interact with gas-phase species through reactions of the form $XCO_3 + 2HY + nH_2O \leftrightarrow XY_2 \cdot nH_2O + CO_2 + H_2O$ (R1), where $X = Ca$ or Mg , $Y = NO_3$ or Cl , and n is the hydration number of the XY_2 salt. Laboratory investigations of R1 ($X = Ca$, $Y = NO_3$) indicate that HNO_3 is irreversibly acquired by $CaCO_3$ to form $Ca(NO_3)_2$ in idealized environments that do not contain CO_2 . However, the atmosphere contains significant concentrations of CO_2 , which could drive R1 in reverse. In the bulk, the XY_2 salts in R1 are known to exist as stable hydrates. However, an expression for the variation of the deliquescence relative humidity (DRH) with temperature for hydrates has not been reported. One goal of this work is to determine the thermodynamically preferred state governed by R1 for atmospheric conditions. A related objective is to derive an expression for the variation of DRH with temperature for hydrates. Equilibrium concentrations of HCl and HNO_3 as functions of temperature and RH were determined for R1 and were compared with ambient measurements from locations that experience high dust loadings. An equation for the temperature dependence of the DRH of hydrated salts was derived by building on previous work for anhydrous salts. Predictions of this expression agree with measurements and indicate that $DRH(T)$ is markedly different for hydrated and anhydrous forms of some common salts. For R1 with stable-hydrated XY_2 , the forward direction is thermodynamically preferred for typical atmospheric conditions. These reactions scavenge HCl and HNO_3 from the gas phase. For R1 with anhydrous XY_2 , the forward direction is prohibited under some atmospheric conditions. R1 containing aqueous-ionized $CaCl_2$ can proceed in reverse under some conditions, and thereby release HCl into the gas phase. Our work suggests that hydrated states of XY_2 should be considered when modeling R1 in low RH situations.