A THEORETICAL AND MODELING STUDY OF VOLATILE CHEMICAL PARTITIONING DURING CLOUD HYDROMETEOR FREEZING

Amy L. Stuart, Texas A&M University
Mark Z. Jacobson, Stanford University

Thunderstorms can significantly impact chemical distributions in the troposphere by 1) redistribution of air and hydrometeors containing trace chemicals and 2) providing a multi-phase environment for chemical phase changes and reactions. Interactions between ice-containing hydrometeors and chemicals are not well understood. Laboratory and field measurements of chemical partitioning during freezing provide greatly varying estimates of the retention efficiency of volatile solutes. In this work, we develop the theory of volatile chemical partitioning during hydrometeor freezing (termed 'freezing retention'), apply it for a variety of freezing conditions and chemicals, and compare the results to available experimental data. By analyzing the hydrometeor-scale processes involved in retention for non-rime freezing, dry-growth riming, and wet-growth riming, we investigated the factors that control it. For non-rime freezing, we developed a theoretical dimensionless number to indicate retention, derived its dependence on conditions and chemical properties, and calculated its value for several freezing cases for SO_2, H_2O_2, NH_3, and HNO_3. Retention is apparently highly chemical specific, controlled largely by the effective Henry's constant (and hence the drop pH for dissociating chemicals). Chemicals with high effective Henry's constants (HNO_3) will be fully retained during freezing, while chemicals with lower effective Henry's constants (SO_2) will undergo some loss. For chemicals that undergo loss, the degree of retention depends on freezing conditions. Retention likely increases with decreasing temperature and exhibits a maximum at intermediate drop sizes and ventilation. For dry-growth riming, we extended the development to predict retention and compared predicted values to experimental data from several measurement studies. The model agrees well with the data and provides a quantitative explanation for the differences in measured retention. For wet-growth riming, we developed a steady-state retention model. It suggests retention is dependent on the fraction unfrozen water in the riming hydrometeor. This work provides theory-based hypotheses regarding the dependence of retention on physical factors and chemical properties that can be used to develop robust parameterization in cloud models.