Understanding Aerosol Chemistry Through Computational Modeling

Belinda Slakman
Department of Chemical Engineering
Northeastern University

Aerosols are heterogeneous mixtures of solid particles or droplets of liquid in a gas. Atmospheric aerosols originate from vehicle and factory pollution as well as dust, and they have significant effects on climate, health, and stability of ecosystems. Thus, it is crucial to further understand the chemistry and kinetics of aerosol formation and aerosol interaction with other molecules. The reaction mechanisms are detailed, and may include hundreds or thousands of different chemical species[1]. It is difficult and error-prone to calculate these complex kinetics by hand.

Recent studies have recognized the need for a modeling approach to understand the formation and growth of aerosols[2,3]. However, these studies are limited by lumped kinetics approaches, use of empirical data, or both. A model which derives reaction pathways solely from first principles is necessary to fully understand these complicated mechanisms and to build a complete reaction network.

The Reaction Mechanism Generator (RMG) is an open-source software tool for predicting kinetic models of large reaction networks. RMG uses chemical knowledge to propose elementary chemical reactions and their rates. The goal of this project is to add aerosol-relevant functionalities to the version of RMG written in Python, which currently works well for gas phase combustion of hydrocarbons.

In this talk, I will discuss adding corrections into RMG for liquid phase reactions to account for solubilties of species in liquid droplets. For every molecule, solute descriptors are determined using a molecular structure group additivity method[4]. Using these solute descriptors, as well as solvent descriptors, partition coefficients between solute and solvent are calculated using Linear Solvation Energy Relationships (LSERs)[5]. The partition coefficients along with the solute and solvent descriptors are then employed to calculate enthalpy, entropy and Gibbs' free energy of solvation for all species. These have been compared to known solvation thermodynamics for molecules in a database.

The next step in this project is to modify reaction kinetics to account for diffusion of gases in aerosol particles. Future work includes adding elements to RMG that are important in atmospheric chemistry, including nitrogen and the halogens, and adding lower temperature rates to RMG's database.

References:

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