Chapter 6

Conclusions

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Organic compounds comprise a substantial fraction of atmospheric particular matter (PM). Predicting the atmospheric gas-particle distribution of organic species and water is important in understanding the formation of secondary organic aerosols (SOA). Gas-particle (G/P) partitioning of any individual organic compound is governed strongly by the vapor pressure of the compound as well as its liquid-phase activity coefficient. Due to the lack of thermodynamic data for the wide range of organics compounds with diverse physical and thermodynamic properties, theoretical estimation methods are required for vapor pressures and liquid-phase activity coefficients.

In Chapter 2 we present a vapor pressure estimation method that makes use of the advances in computational and theoretical chemistry. The method is based on atomistic simulations combined with the Clausius-Clapeyron equation. Vapor pressures of the five dicarboxylic acids: malonic (C_3), succinic (C_4), glutaric (C_5), adipic (C_6), and pimelic (C_7), are predicted using the derived Clausius-Clapeyron equation. We focus on dicarboxylic acids because of their particular importance as ubiquitous components of atmospheric aerosols. We show that heats of vaporization can be estimated from calculated cohesive energy densities (CED) of the pure compound obtained from multiple sampling molecular dynamics. The heats of vaporization of five dicarboxylic acids: malonic (C_3), succinic (C_4), glutaric (C_5), adipic (C_6), and pimelic (C_7) at 500K are in agreement with experimental values with an averaged error of about 4%. Predicted heats of sublimation for $C_3 - C_7$ dicarboxylic at 298 K agree reasonably with experimental data, with a maximum average error of 17%. Predicted liquid vapor pressures agree well with available literature data with an averaged error of 29%. While the predicted solid

vapor pressures at ambient temperature differ considerably from literature values (an averaged error of 71.5%), we are able to capture qualitatively the odd-even alternation. Overall, the predictions are considered satisfactory given the simplicity of the method and the substantial uncertainty involved in the low-pressure data.

Quantum mechanical (QM) methods were also used to investigate the thermodynamic feasibility of various acid-catalyzed aerosol-phase heterogeneous chemical reactions in Chapter 3. Although experimental studies have provided convincing evidence that aerosol-phase reactions, such as hydration, polymerization, hemiacetal/acetal formation, and aldol condensation can lead to additional formation of secondary organic aerosol (SOA), uncertainty remains as to the likely aerosol-phase chemical reactions involving absorbed gas-phase organic compounds. A stepwise procedure is presented to determine physical properties such as heats of formation, standard entropies, Gibbs free energies of formation, and solvation energies from quantum mechanics, for various short-chain aldehydes and ketones. Quantum mechanical gas-phase Gibbs free energies of formation compare reasonably well with the literature values with a root mean square (RMS) value of 1.83 kcal/mol for the selected compounds. Equilibrium constants (reported as log K) of hydration reactions and aldol condensation are then determined for formaldehyde, acetaldehyde, acetone, butanal, hexanal, and glyoxal; predictions are in qualitatively agreement with previous studies. The QM results for glyoxal reactions are also consistent with experimental observations. In the evaluation of thermodynamic tendency of various reactions, where the emphasis is not on the absolute but relative changes in free energies, we have shown that quantum

methods can serve as useful tools for first approximation, especially for species with no available data.

Within an atmospheric particle, liquid and solid phases can exist at equilibrium, a version of the UHAERO thermodynamic model that includes organic/water systems is presented (Chapter 4). Phase diagrams for a number of model organic/water systems characteristic of both primary and secondary organic aerosols are computed. The effect of organic phase equilibria on inorganic deliquescence behavior are shown in the deliquescence phase diagrams of $(NH_4)_2SO_4/H_2SO_4/NH_4NO_3/HNO_3/H_2O$ when the system also includes two organic species, with sulfate fractions (Y) of 1 and 0.85. In the presence of organic species, the system can exhibit a mixture of multiple liquid and solid phases, depending on the relative composition of inorganic and organic species, RH, and temperature. However, a fully crystalline state of the system is not permissible. Three different sets of UNIFAC parameters used in the study, and the sensitivity of a predicted phase diagram to these different sets of UNIFAC parameters are evaluated. The method affords a rigorous computation of inorganic/organic/water phase equilibria. While such liquid/solid phase equilibrium computations may not be necessary in a 3D atmospheric chemical transport model, the results of the UHAERO model are a benchmark to which more approximate thermodynamic models may be compared.

The main parameter in the gas-particle partitioning and phase equilibrium calculation is the estimation of the activity coefficients as a function of the liquid phase composition. We evaluate in Chapter 5 the performance of four recent activity coefficient models developed for inorganic-organic-water mixtures typical of atmospheric aerosols. The CSB model and the ADDEM model treat ion-water and organic-water interactions

but do not include ion-organic interactions; these can be referred to as "decoupled" models. The other two models, Ming and Russell and X-UNIFAC.3, include ion-organic interactions; these are referred to as "coupled" models. Based on the comparisons between predicted and experimental water activities, it is found that the decoupled models perform as well as, and in some cases better than, the coupled models. For coupled models, the scarcity of experimental data for mixtures of atmospheric relevance remains a limitation for testing activity coefficient models. Decoupled models offer the advantage in the flexibility of the choice of activity coefficient model. Even in the absence of mixture parameters, decoupled models such as the CSB and ADDEM models, produce predictions that are in excellent agreement with experimental data for most systems for low to moderately concentrated solutions. At present, decoupled approaches, such as those in CSB and ADDEM, are generally more preferable than the coupled models. However, it should be remembered that the ion-organic interaction parameters can improve model performance, and the mixture parameters are probably important in representing solutions with high solute concentrations. When experimental data become available, further development in the application of the ion-organic parameters should be considered.