

THERMODYNAMIC MODELING OF ORGANIC AEROSOL

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Abstract

Modeling atmospheric aerosols containing a large organic fraction with unknown chemical composition and properties has been a constant challenge. The dissertation focuses on the theoretical treatment of the thermodynamic equilibrium of atmospheric aerosol involving organic species.

We present a vapor pressure estimation method, based on quantum chemistry methods, to predict the liquid vapor pressure, enthalpies of vaporization, and heats of sublimation of atmospheric organic compounds. Predictions are compared to literature data, and the overall accuracy is considered satisfactory given the simplicity of the equations. Quantum mechanical methods were also used to investigate the thermodynamic feasibility of various acid-catalyzed aerosol-phase heterogeneous chemical reactions. 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. Equilibrium constants of hydration reactions and aldol condensation are then reported; predictions are in qualitative agreement with previous studies. We have shown that quantum methods can serve as useful tools for first approximation, especially for species with no available data, in determining the thermodynamic properties of multifunctional oxygenates.

We also present an atmospheric aerosol phase equilibrium model to determine the aerosol phase equilibrium of aqueous systems. Phase diagrams for a number of organic/water systems characteristics of both primary and secondary organic aerosols are

computed. Effects of organics on the deliquescence behavior of electrolytes are also shown in the inorganic/organic/water phase diagrams.

Finally, we evaluate the performance of four recent activity coefficient models developed for inorganic-organic-water mixtures typical of atmospheric aerosols. Based on the comparison on water activities, it is found that models that include ion-organic mixture parameters (referred to as coupled models) do not necessarily produce more accurate predictions than those models that utilizes additive approaches (referred to as decoupled models). Since the chemical composition and physical properties of the organic fraction is largely unknown, the additive approaches of the decoupled models are more feasible than the coupled models.

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Chapter 1

Introduction

Introduction

Organic species are ubiquitous constituents of atmospheric particular matter [1, 2]. Organic aerosol is emitted directly from sources, or formed in the atmosphere from the gas-phase oxidation of volatile organic compounds (VOCs), oxidation products of VOCs usually have sufficiently low vapor pressures that they partition into the condensed phase, forming secondary organic aerosol (SOA). Atmospheric aerosols generally contain both inorganic components and an organic fraction comprising a wide range of organic compounds of diverse physical and chemical properties. Water and volatile species are distributed between the gas and aerosol phases, governed by thermodynamic equilibrium. The common form of the gas/particle (G/P) partitioning constant (K_p) for absorptive uptake into the particle phase is [3, 4]:

$$K_{p,i} = \frac{(\text{ng}/\mu\text{g})_{\text{particle phase}}}{(\text{ng}/\text{m}^3)_{\text{gas phase}}} = \frac{F_i/TSP}{A_i} = \frac{760RTf_{om}}{10^6 MW_{om}\xi_i p_{L,i}^0} \quad (1.1)$$

where $p_{L,i}^0$ (torr) is the compound's vapor pressure as a pure liquid (subcooled if necessary); ξ_i is the activity coefficient of species i in the particle phase; A_i (ng m^{-3}) is the concentration of species i in the gas phase; F_i (ng m^{-3}) is the concentration in the aerosol phase; TSP ($\mu\text{g m}^{-3}$) is the total suspended particulate matter (PM) concentration; R is the ideal gas constant ($8.2 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$); T (K) is temperature; f_{om} is the weight fraction of the TSP that comprises the absorbing organic matter (OM) phase; MW_{om} (g mol^{-1}) is the number average molecular weight of the absorbing OM phase. The importance of $p_{L,i}^0$ and ξ_i in controlling G/P partitioning is evident in equation 1.1.

Low vapor pressures values are extremely difficult to measure by experiments. Furthermore, many organic compounds are solids in their pure form at ambient temperature. Even if the vapor pressures can be measured, the solid vapor pressures, $p_{S,i}^0$,

still need be adjusted to the corresponding subcooled p_L^0 values. As a result, the p_L^0 values of most atmospheric-relevant compounds are not known.

As an alternative to experimental measurements, interest is gaining in computational methods that predict p_L^0 based on multiparameter correlations between structure and p_L^0 , such as the UNIFAC-based method by Asher et al. [5]. In Chapter 2 a method based on quantum chemistry methods combined with the Clausius-Clapeyron equation to predict the liquid vapor pressure, enthalpies of vaporization, and heats of sublimation of atmospheric organic compounds, is presented. Vapor pressures of the five dicarboxylic acids, malonic, succinic, glutaric, adipic, and pimelic acids, are then predicted using the derived Clausius-Clapeyron equation.

Experimental studies have provided convincing evidence that aerosol-phase heterogeneous chemical reactions (possibly acid-catalyzed) are involved to some extent in the SOA formation. In Chapter 3 the quantum mechanics (QM) methods are used to determine physical properties such as heats of formation, standard entropies, Gibbs free energies of formation, and solvation energies, for various short-chain aldehydes and ketones. These QM results are then used to determine the equilibrium constants (reported as $\log K$) of aerosol-phase chemical reactions, including hydration reactions and aldol condensation for formaldehyde, acetaldehyde, acetone, butanal, hexanal, and glyoxal. The results are potentially useful in determining the relative thermodynamic tendency for atmospheric aerosol-phase reactions.

Water, volatile inorganic and organic species are distributed between the gas and aerosol phases according to the gas/particle thermodynamic equilibrium. Liquid and solid phases can exist at equilibrium within an atmospheric particle. Models exist for

computation of phase equilibria for inorganic/water mixtures for atmospheric aerosols. When organic species are present, the phase equilibrium calculation within the aerosol phase is complicated by organic/water interactions as well as the potentially large number of organic species. Chapter 4 presents an atmospheric aerosol phase equilibrium model, an extension of the UHAERO inorganic thermodynamic model [6], to determine the phase equilibrium of organic-water systems. Phase diagrams for a number of model organic/water systems characteristic of both primary and secondary organic aerosols are computed. Also calculated are inorganic/organic/water phase diagrams that show the effect of organics on inorganic deliquescence behavior.

Activity coefficients are important in the calculation the gas/phase partitioning equilibrium and the phase equilibria within the particle phase. Hence, considerable effort has been devoted to develop activity coefficient models that can be applied to mixed organic-electrolyte-water mixtures. Several existing activity coefficient models are examined in Chapter 5. Calculated water activities are compared with experimental data for various organic and organic-electrolyte solutions. In addition, the strengths and weaknesses of each approach are discussed.

In Chapter 6 a summary is given for the results presented in the previous sections. The Appendix presents calculations of the entropy information for common amine systems using classical and quantum simulations.

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