

Combined Quantum Mechanics, Atomistic Simulation and Thermodynamic Frameworks for Vapour-Liquid Equilibrium Systems with Chemical Reactions in One of the Phases: Molten Salt/Ionic Liquid VLE and CO₂ Post-Combustion Reactive Absorption as Examples

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Chemically reacting systems are ubiquitous in industrial settings and in nature, but their vapour-liquid equilibrium (VLE) speciation and vapour pressure properties have been studied only sparsely by means of molecular simulation methodology. Two important examples are pure molten salts and pure ionic liquids in equilibrium with their vapour phases, and a non-reacting flue gas containing CO₂ in equilibrium with a reactive solvent. The vapour composition and pressure of a high-temperature molten salt is an important property in the design of energy storage systems in the solar power and nuclear industries, and the CO₂ solubility of a flue gas containing a specified partial pressure of CO₂ is an important property in the design of post-combustion CO₂ capture systems. For both types of systems, the relevant vapour pressures are small and an ideal-gas assumption is often an adequate approximation. However, modeling these systems is challenging due to the presence of chemical reactions, respectively in the gas phase for molten salts and in the liquid phase for CO₂ solvents.

In this talk, I will describe recent successful treatments of both types of problem, based upon the use of macroscopic thermodynamic models of the involved electrolyte systems, and the calculation of the thermodynamic model parameters by means of a combination of quantum mechanics and atomistic modeling. This leads to a purely predictive framework that requires no experimental data for its implementation. I will also express my personal opinion that the perceived difficulty of treating such problems is due to the way that macroscopic thermodynamics is conventionally taught to students, and suggest an alternative teaching approach.