172b Monte Carlo Simulation of Equilibrium Reactions at Vapor-Liquid Interfaces

Heath Turner

Chemical reactions are known to behave differently, depending upon their local environment. While the interactions with neighboring molecules may alter both the kinetics of chemical reactions and the overall equilibrium conversion, we have performed simulations of the latter. The particular environment that we address is the vapor-liquid interface, since only a few, limited studies have explored the influence of an interface on equilibrium reaction behavior. Previous investigations of reaction equilibrium at interfaces have only dealt with simple association behavior and isomerization reactions. In this work, simple dimerization reactions are modeled, as well as more complex multi-component reactions, using the reactive Monte Carlo simulation technique. We find that the conversion of a reaction can be markedly different at an interface as compared to the bulk vapor and liquid phases, and these trends are analyzed with respect to specific intermolecular interactions. In conjunction, we calculate the surface tension of the reacting fluids at the interface, which is valuable for understanding a broad range of important chemical and biological systems. To the best of our knowledge, this work represents the first application of the reactive Monte Carlo method to study fluid interfaces, as well as the first simulation study to predict the vapor-liquid surface tension of reacting fluids. The first reaction that we simulate is a simple Lennard-Jones model, which is used to understand the effect of the interaction parameters on both conversion and surface tension across the vapor-liquid interface. The second reaction is modeled as a more realistic dimerization, with parameters chosen to accurately model nitric oxide dimerization: $NO + NO = (NO)2$. Finally, we incorporate more complex reaction behavior by modeling the equilibrium of $Br2 + Cl2 = 2BrCl$. In all three studies, interfacial composition profiles, surface tension measurements, and reaction conversions are analyzed. We have found that the A/B equilibrium, NO dimerization, and BrCl reaction equilibrium all seem to follow similar trends at their vapor-liquid interfaces, when analyzed with respect to their intermolecular potentials. As a consequence, the reaction equilibrium tends to shift in the direction that minimizes the surface tension, depending on the intermolecular parameters of a particular system. In tandem, as the surface tension increases, the magnitudes of the equilibrium shifts are more dramatic. While our calculations are based on results from only three systems, we plan to confirm these trends in the future with other reacting systems.