

# Exploring Multicomponent Phase Equilibria by Monte Carlo Simulations: Towards a Description of Gas-Liquid Chromatography

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The calculation of retention times, retention indices, and partition constants is a long sought-after goal for theoretical studies in gas chromatography. Although advances in computational chemistry have improved our understanding of molecular interactions, little attention has been focused on chromatography, let alone calculations of retention properties. Configurational-bias Monte Carlo simulations in the Gibbs ensemble have been used to calculate single and multi-component phase diagrams for a variety of hydrocarbon systems. Transferable force fields for linear and branched alkanes have been derived from these simulations. Using calculations for helium/n-heptane/n-pentane systems, it is demonstrated that this approach yields very precise partition constants and free energies of transfer. Thereafter, the partitioning of linear and branched alkane solutes (with five to eight carbon atoms) between a squalane liquid phase and a helium vapor phase is investigated. The Kovats retention indices of the solutes are calculated directly from the partition constants.