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Isotopic Effect on Phase Equilibria of Pure Fluids and Mixtures: Molecular Simulation, Theory and Experiment

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The temperature dependence of vapor – liquid and vapor – solid isotope fractionation factors was predicted by NVT-Molecular Dynamics and Gibbs Ensemble Monte Carlo simulations for atomic molecules ($^{36}Ar/^{40}Ar$, $^{20}Ne/^{22}Ne$, $^{80}Kr/^{84}Kr$) to assess the accuracy of $\hbar^2-$order Kirkwood-Wigner free energy expansion for specific Lennard – Jones parameterizations. In addition, the composition dependence of the corresponding fractionation factors for binary $Ar-Kr$ mixtures was also predicted. Our simulation results compare very well with the existing experimental data. Fractionation factors were also predicted for other isotopic pairs, which have not been studied experimentally to date, including $^{20}Ne/^{21}Ne$, and $^{132}Xe/^{136}Xe$. Some premises behind the microscopic interpretation of the fractionation factors are also tested. Relevant extensions of this study to polyatomic molecular systems of geochemical interest, including O_2, N_2, CO, and H_2O, are also discussed. The advantages of this approach over quantum mechanical calculations and the limitations of the methodology are addressed as well.

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Reference

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