

Simulating Vapor–liquid Equilibria of PH₃, AsH₃ and SbH₃ from First Principles

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Abstract

Due to their toxicity, flammability, and chemical instability, the vapor–liquid equilibria of the group V hydrides, phosphine, arsine, and stibine, are under-explored. Gibbs ensemble Monte Carlo simulations were performed to obtain the vapor–liquid coexistence curves (VLCCs) for PH₃, AsH₃, and SbH₃ using Kohn-Sham density functional theory with two popular generalized gradient approximation functionals to describe the inter- and intramolecular interactions. In conjunction with the third-generation dispersion correction of Grimme, Goedecker-Teter-Hutter pseudopotentials, and double- ζ valance polarization basis sets, the Perdew-Burke-Ernzerhof (PBE) and Becke-Lee-Yang-Parr (BLYP) exchange-correlation functionals yield critical temperatures for PH₃ of 342 ± 8 and 289 ± 12 K, respectively, that over/under predict the experimental value by about 20 and 35 K. The high computational cost of first principles simulations necessitates relatively small system sizes and short simulations that can lead to problems near the critical point. No significant system size effects were observed for the VLCC and liquid structure of PH₃. For AsH₃ and SbH₃, the predicted

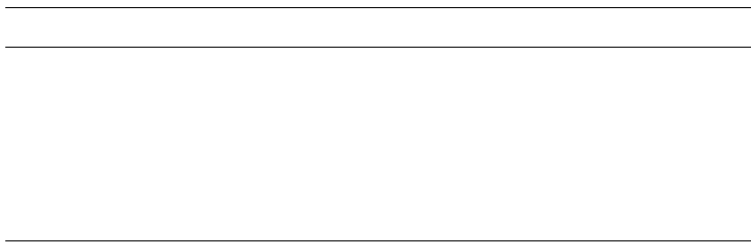
critical temperatures with the PBE exchange-correlation functional are close to 450 K, a value about 20% above the available literature value for AsH .

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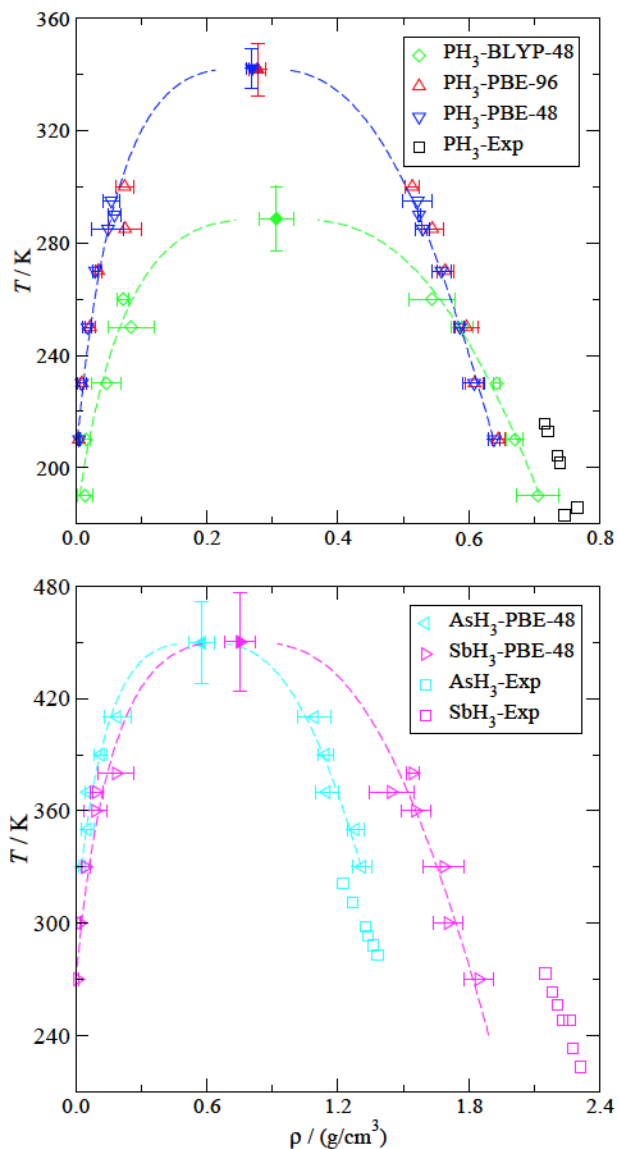
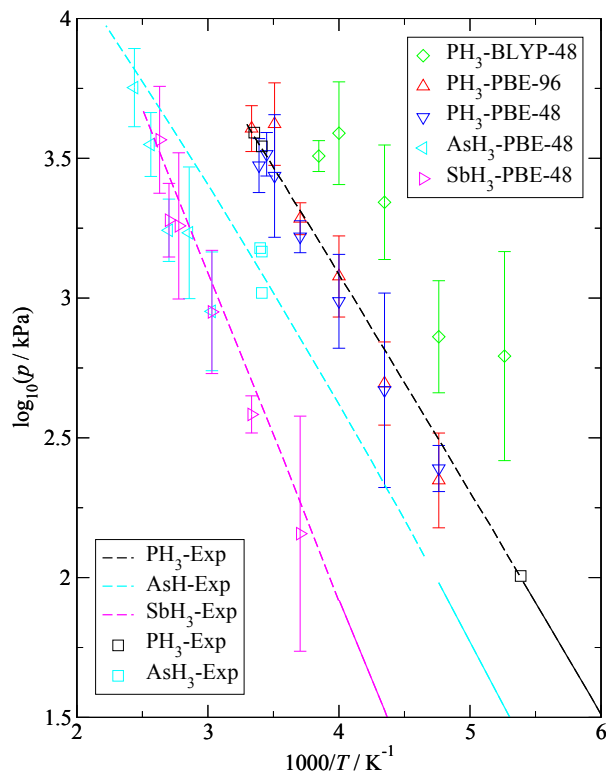


Figure 1: Vapor-liquid coexistence curves for PH_3 (top) and AsH_3 and SbH_3 (bottom). Dashed lines and filled symbols represent fits to the scaling law and the calculated critical points. Experimental liquid densities are taken from Refs.^{8,9,37-41}

there is some confidence in the predicted critical temperature of 450 ± 26 K for molecular SbH_3 . Here it should be noted that it is the critical point of molecular SbH_3 that is needed as input for an equation of state, i.e., chemical decomposition should not be included in such predictions.⁴⁸

In contrast to the fairly accurate predictions found here for PH_3 and SbH_3 , the predictions obtained with the PBE exchange-correlation functional for arsine do not follow the same



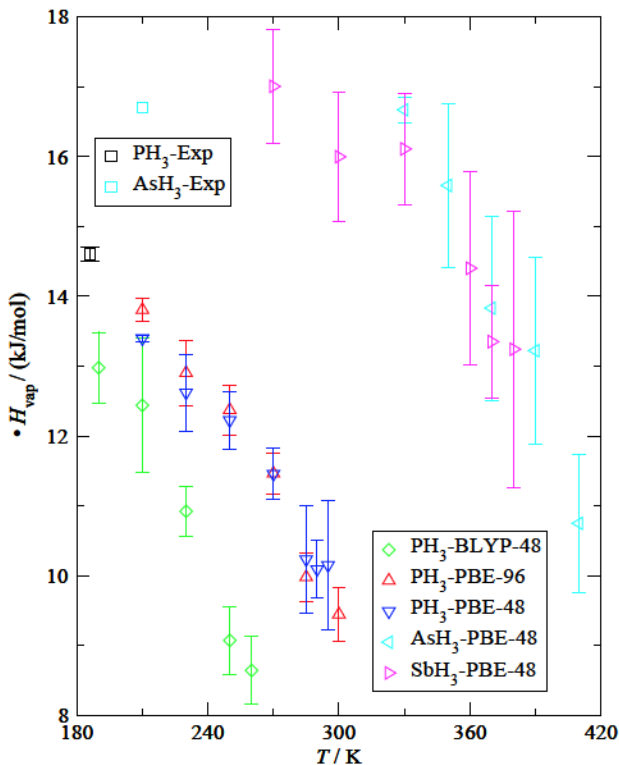
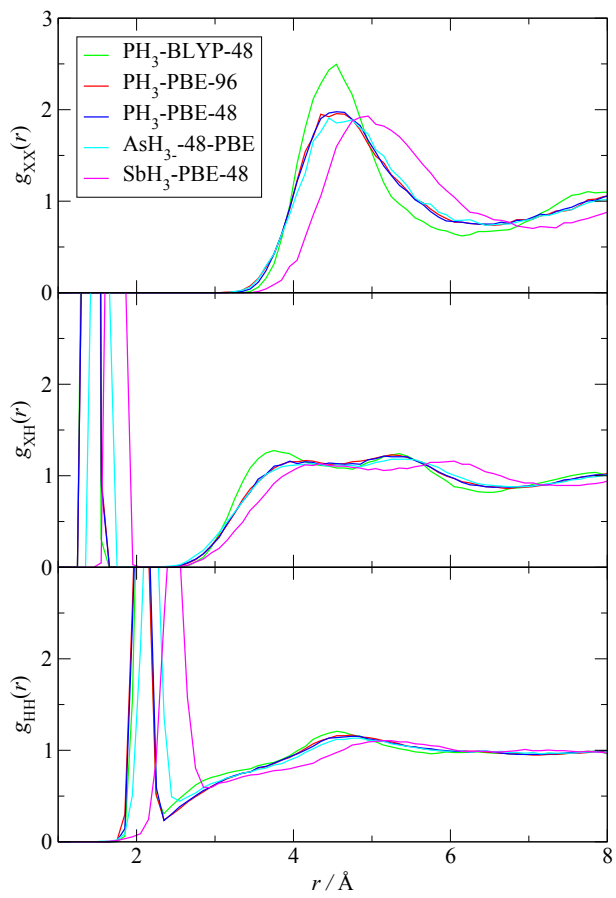


Figure 3: Heat of vaporization versus temperature for all systems. Experimental data are taken from Refs. ^{44,47}

(bond length and bending angle) of PH_3 , AsH_3 , and SbH_3 obtained for the liquid phase are illustrated in Figure S4. In general, neither of these properties shows a significant change with increasing temperature. Notably, the H–X–H bend angles for these higher group V hydrides are closer to 90° than to the tetrahedral angle found for ammonia and also water.⁴⁹ For PH_3 , the PBE and BLYP functionals yield P–H bond lengths of 1.432 and 1.428 Å, respectively, that are slightly longer than the experimental gas-phase value of 1.419 Å,⁴⁹ whereas the H–P–H angles of 92.5° and 93.1° for the PBE and BLYP functionals, respectively, are slightly smaller than the experimental gas-phase value of 93.7° .⁴⁹ Similar trends are also observed for AsH_3 and SbH_3 , but the deviations in the X–H bond length of 1.550 and 1.745 Å predicted by the PBE functional are somewhat larger compared to the experimental gas-phase values of 1.523 Å⁴⁹ and 1.710 Å,⁵⁰ respectively, whereas the differences in the H–X–H bending angle are similar (AsH_3 : 90.2° versus 91.34° ;⁴⁹ SbH_3 : 90.7° versus 91.42° ⁵⁰).

The X–X, X–H, and H–H radial distribution functions (RDFs) for all five XH_3 systems



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Stibine

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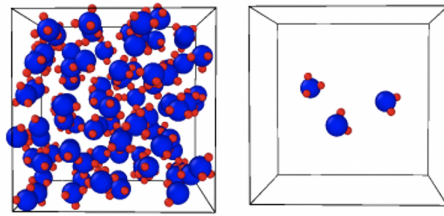
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PH_3 at $T = 250 \text{ K}$