The Representation of Cross Second Virial Coefficients by Multi-Fluid Mixture Models and Other Equations of State

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It is well-known that the cross second virial coefficient B_{12} is only a function of temperature and does, therefore, not depend on the composition of the mixture. However, many commonly used mixture models do not necessarily fulfil this condition. In this work, we compare the results of multi-fluid mixture models for B_{12} with accurate experimental data for mixtures of methane + propane, argon + carbon dioxide, hydrogen + carbon dioxide, and ethane + carbon dioxide. It was found that neither multi-fluid mixture models with adjusted parameters nor multi-fluid mixture models employing a theoretically-based departure function using either UNIFAC or COSMO-SAC as g^{E} -model are capable of describing the cross second virial coefficient correctly. Furthermore, values for B_{12} calculated with other commonly used equations of state (SRK, PSRK, and PCP-SAFT), which are available in the thermophysical property software TREND 4.0, have been evaluated and were also compared to the experimental data. Among these models, only the SRK with quadratic mixing rules for the attraction parameter and linear mixing rules for the co-volume yields the physically correct behavior for B_{12} . A possible modification of the multi-fluid mixture model in the limit of zero density for achieving the correct behavior of the cross second virial coefficient is discussed.