

Adjusting the Parameters of the van der Waals Equation of State for Liquid-Phase p - v - T Predictions

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A simple equation of state (EoS) with only two or three parameters is not capable of accurately describing the pressure-molar volume-temperature (or p - v - T) behavior of a fluid over a wide range of temperatures and pressures that might include both the vapor and liquid phases. As a result, the parameters for equations of this kind are usually adjusted to provide optimum accuracy for a specific task involving a much narrower range of temperatures and pressures. Thus, if vapor-phase p - v - T predictions are to be carried out, virial coefficients of the vapor at appropriate temperatures could be employed to determine the EoS parameters. In situations where the saturation curve, the coexistence curve, or either of the spinodal curves is to be predicted, the EoS parameters are generally calculated from more traditional methods involving the critical constants of the fluid.

Neither of the above approaches will, however, yield accurate results if they are employed for the purpose of liquid-phase predictions. In this situation liquid-state data should be used to determine the EoS parameters. We have carried out a preliminary exploration of the use of liquid density, isobaric expansivity, and isothermal compressibility data for this purpose. The approach was applied to the parameters in the van der Waals EoS for liquid argon. EoS molar volume predictions are compared to experimental data and to predictions based on the various ways that critical data can be used to determine EoS parameters. As expected, this new approach is found to yield p - v - T predictions that are far superior to those of the methods that employ critical data.