2.12 Summary

The equation of state is a fundamental property of fluids that describes the relationship between molar volume, temperature, and pressure. This relationship is expressed mathematical as an equation between V, P, and T, or alternatively, between Z, P, and T. The PV graph is graphical representation of this relationship and a convenient way to present the phase behavior of a pure component. It is a good idea to draw a qualitative PV graph when solving problems involving heating, cooling, compression, or expansion of pure fluids, as a way of becoming oriented in thermodynamic space. Simple processes on this graph is represented by simple paths and help visualize any phase transformations that may occur.

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The accurate prediction of the molar volume, or, equivalently, of the compressibility factor, is a requirement in engineering calculations. Several methodologies were discussed in this chapter:

- *Tabulated values.* Tabulations are available for a large number of pure components. The steam tables is one such example. Usually, however, property tabulations are not as detailed or extensive as the steam tables. Tables are generally the most accurate source for properties. They are not convenient, however, for large-scale calculations.

- *Generalized graphs.* These graphs are correlations based on corresponding states. Using just three physical constants, critical pressure and temperature, and acentric factor, one can estimate the molar volume of a pure fluid over a very wide range of conditions. This is a very important advantage but it comes with certain limitations. The method is approximate and is based on graphs that have been tweaked to provide overall good accuracy for several different fluids. Necessarily, the agreement will be better for some and worse for others. The method should be used only for normal fluids that are not polar to a significant degree. This covers a large number of compounds but excludes many industrially important molecules, chiefly among them, water.

- *Equations of state.* An equation of state in mathematical form has the advantage that it can be used in repetitive calculations and is especially suited for computer-based calculations. Industrial software for chemical process design makes extensive use of such equations. The equations discussed in this chapter (van der Waals, Soave-Redlich-Kwong, and Peng-Robinson) incorporate the principle of corresponding states in their constants, which can be computed