

18 MULTIPARAMETER EQUATIONS OF STATE

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18.1 INTRODUCTION

Accurate thermophysical properties of fluids are needed for the development of reliable mathematical models of energy systems. Although significant improvements are being made in predicting thermodynamic properties of pure fluids and mixtures using theory-based methods, there is a need for more accurate equations of state both for applications in engineering system design and analysis and to satisfy scientific data needs. Current practice in the development of computer programs, property tables, and charts involves the correlation of selected experimental data for a particular fluid or mixture using a model which is accurate for calculating properties over a wide range of pressures and temperatures.

Throughout this chapter the word "data" is used to refer to experimental measurements. The term "property formulation" is the set of equations used to calculate properties of a fluid at specified thermodynamic states defined by an appropriate number of independent variables. A typical thermodynamic property formulation is based on an equation of state which allows the correlation and computation of all thermodynamic properties of the fluid, including properties such as entropy that cannot be measured directly. In this work, the general term "equation of state" is used to refer to the empirical models developed for calculating fluid properties. The term "fundamental equation" is often used in the literature to refer to empirical descriptions of one of four fundamental relations: internal energy as a function of volume and entropy, enthalpy as a function of pressure and entropy, Gibbs energy as a function of pressure and temperature, and Helmholtz energy as a function of density and temperature. Modern equations of state for pure fluid properties are usually fundamental equations explicit in the Helmholtz energy as a function of density and temperature. All thermodynamic properties may be calculated without additional ancillary equations for saturation properties through the use of the Maxwell criterion (equal pressures and Gibbs energies at constant temperature during phase changes).

The development of an accurate property formulation requires analysis of the available data and correlation using a suitable functional form. The process of determining the optimum correlation often involves considerable art in addition to science, and experience plays a significant part in the determination of the final result. The objective of the correlator is to ascertain the accuracy of the available experimental data for the particular fluid or system under investigation, and to develop a mathematical model capable of representing the data within the reported or estimated experimental uncertainty. The practical models of today are empirical or semi-empirical in nature, although virtually all are based upon sound theoretical principles. The limitations of the model selected must be mutually understood by the correlator and the user for effective system optimization and related work.

Thermodynamic relationships can be used to calculate (or derive) various properties using an equation of state once a state has been specified by an appropriate number of independent properties. Such calculations require either mathematical integration or differentiation of the equation of state. Reference states, or datum states, are defined for enthalpy and entropy to allow numerical values of entropy or characteristic energies with respect to these datum states. While properties of solid-liquid equilibrium states are usually still correlated separately, equations of state are generally fitted to vapor-liquid equilibrium properties. An accurate description of the Maxwell criterion is important for consistent description of enthalpies and internal energies at liquid states.

18.2 THE DEVELOPMENT OF A THERMODYNAMIC PROPERTY FORMULATION

The importance of accurate experimental data in the development of a thermodynamic property correlation is well established. Any systematic errors in experimental data sets will be reflected in the quality of the correlation based upon such data. If data are not available for a particular region of the surface, it is often helpful to use predicted values in the fitting process. Such predictions can be verified or discounted later when experimental data are available.

There are several fixed points, reference state properties and molecular data which should be available for each fluid for which a thermodynamic-property correlation is developed. These include the temperature, density, and pressure at the critical point and triple point, the molecular weight, the molar gas constant, and the enthalpy and entropy reference values mentioned previously.

The following experimental data are generally considered essential in developing an accurate equation of state: vapor pressure, saturated liquid density, ideal-gas heat capacities expressed as functions of temperature, and p - ρ - T data in all regions of the thermodynamic surface. Saturated vapor density values obtained from experiment (or derived from other data using theoretical methods) are essential if linearized phase-equilibrium data are used in linear algorithms during the development of an equation of state. Highly accurate speed-of-sound data from spherical resonators have recently become important for the development of accurate equations of state. The accuracy of calculated energies and caloric properties can be improved if the following data are also available: c_V - ρ - T (isochoric heat capacity), c_P - p - T (isobaric heat capacity), Δh - p - T (enthalpy differences), and Joule-Thomson coefficients.

Correct behavior of the equation of state in the critical region is often a concern of users of property formulations. Classical equations cannot represent the theoretically expected nonanalytical behavior at the critical point. However, state-of-the-art multiparameter equations of state are sufficiently accurate in the critical region to satisfy most data needs (although they should not be used as basis for theoretical calculations regarding the limiting behavior at the critical point). Older or less accurate multiparameter equations of state may show significant shortcomings with regard to the representation of properties in the critical region.

Accuracy and thermodynamic consistency in a wide-range equation of state for a pure fluid imply the following:

1. All thermodynamic properties can be calculated within the limits of experimental uncertainty by differentiating or integrating the equation of state, *i.e.*, arbitrary corrections to derived properties are not required;
2. The equation of state reduces to the ideal gas equation of state in the limit as $p \rightarrow 0$;
3. The equation of state obeys the Maxwell criterion (equal Gibbs energies for saturated liquid and saturated vapor states at a given saturation temperature and the corresponding vapor pressure);
4. The critical region ($\pm 0.25\rho_c$ and $\pm 0.05T_c$) behavior is reasonably consistent with experimental measurements and theoretical considerations except at and very near the critical point;

5. The behavior of calculated constant property lines on the surface of state is consistent with available experimental data and with theoretical predictions (*e.g.*, isotherms should not intersect at high pressures).

An important attribute of an equation of state for engineering applications is relative simplicity, resulting in minimal computation time for calculation of the necessary properties. Although the use of readily developed software has become common in engineering applications, applications which require user specific software developments are still frequent. The use of equations of state which are integrated in the microprocessor code of flow computers, for example, requires fast and compact programs in special languages. If accuracy requirements or demands with regard to the range of validity can be relaxed, shorter equations of state with specified levels of accuracy may be developed to reduce computation times.

In studies to determine equations of state for fluids, a number of empirical polynomial and exponential forms have been suggested for use in fitting experimental measurements. Generally, experimental data are represented by a convenient functional form using linear or nonlinear least-squares curve fitting. The methods used by correlators in developing accurate multiparameter equations of state vary widely depending upon the intended use of the equation being developed. Methods for establishing a rational choice of terms to be included in an equation of state with a large number of adjustable coefficients is outlined in Section 18.3.4. The methods discussed here are generally applicable in studies to determine an optimum functional form for fitting an equation to a large number of data points. Statistical analysis of the results of the least-squares fit to determine a thermodynamic equation of state is useful to guide the correlator. Such analysis should be confirmed by the calculation of properties from the formulation for direct comparison to experimental data.

18.3 THE USE OF LEAST-SQUARES FITTING IN DEVELOPING AN EQUATION OF STATE

18.3.1 The Least-Squares Method

Experimental data are conveniently represented by a model using a selected functional form by linear or nonlinear least-squares curve fitting. Common functional forms are discussed in Sections 18.4 through 18.7. The techniques which are required to establish empirical equations of state were recently explained in detail by Span (1). The theoretical foundation for the application of nonlinear fitting techniques to equations of state is given by Ahrendts and Baehr (2). These methods allow accurate representation of thermodynamic data if care is taken to minimize the inherent ill-conditioning of the matrix associated with fitting equations of state containing relatively large numbers of terms to large selected measured data sets. The general least-squares problem is outlined below. The method is described using the pressure explicit equation form for simplicity. Standard references on statistical methods may be consulted for additional details.

The data considered here are experimental thermodynamic pressure-density-temperature (p - ρ - T) data, denoted as $[(p_1, \rho_1, T_1), (p_2, \rho_2, T_2), \dots, (p_n, \rho_n, T_n)]$. A functional relationship between the data variables is assumed, *i.e.*, $f(\Theta_1, \dots, \Theta_j, \rho, T)$, where $(\Theta_1, \dots, \Theta_j)$ are the coefficients of the terms in the equation used to represent the data. Numerical estimates of the coefficients may be calculated by minimizing the sum of the squares of the residuals between π_i (a function of p_i) and the value of $f(\Theta_1, \dots, \Theta_j, \rho_i, T_i)$. If the exact functional relationship between ρ , T , and π is known, the minimum-variance estimate of Θ_j is obtained by minimizing

$$\left[\pi_1, \dots, \Theta_j, \rho_i, T_i \right]^2 \quad (18.1)$$

function is minimized by requiring

$$\frac{\partial}{\partial \Theta_k} \left[\sum_{i=1}^n \left[\pi_i - f(\Theta_1, \dots, \Theta_j, \rho_i, T_i) \right]^2 \right] = 0 \quad k = 1, 2, \dots, j \quad (18.2)$$

where j is the number of terms (each with one adjustable coefficient) in the equation being developed. This results in j equations with j unknowns.

Since errors of measurement in p - ρ - T data vary among experiments and are different in various thermodynamic regions (*e.g.*, liquid or vapor phases), a procedure of weighting data for use in fitting is highly recommended, even when fitting an equation of state to only p - ρ - T data. Weights are usually calculated according to the law of propagation of variance (the error-propagation formula) in a form similar to

$$\text{weight} = \frac{1}{\sigma_{\pi_i}^2} \quad (18.3)$$

$$\sigma_{\pi_i}^2 = \sigma_{\rho_i}^2 + \left(\sigma_{\rho_i} \frac{\partial f}{\partial \rho_i} \right)^2 + \left(\sigma_{T_i} \frac{\partial f}{\partial T_i} \right)^2 \quad (18.4)$$

where σ_{ρ_i} , σ_{T_i} and σ_{π_i} are estimates of the uncertainty of the experimental data and $\sigma_{\pi_i}^2$ is the calculated variance of the quantity used as a fit variable in the least-squares process.

The new function to be minimized is then

$$\sum_{i=1}^n \left[\frac{\pi_i - f(\Theta_1, \dots, \Theta_j, \rho_i, T_i)}{\sigma_{\pi_i}} \right]^2 \quad (18.5)$$

Taking derivatives of this equation, similar to Equation (18.2), results in j equations with j unknowns. These equations can be written in matrix form as

$$[X][\Theta] = [y] \quad (18.6)$$

When this matrix problem is solved, the resulting Θ_j are estimates of the coefficients for the weighted least-squares fit. Variables are frequently reduced or non-dimensionalized to simplify the use of the resulting equation in different applications. The extension of this discussion to equations explicit in Helmholtz energy (*e.g.*, $a=a(\rho, T)$ or nondimensional equivalents), to the simultaneous consideration of different properties, and to the consideration of properties which depend nonlinearly on derivatives of the dependent variable of the established equation of state is relatively straightforward.

18.3.2 Multiproperty Fitting

A multiparameter equation fitted to p - ρ - T data alone may provide an acceptable representation of the p - ρ - T surface; however, such an equation will neither represent vapor-liquid phase equilibria nor caloric properties in the liquid phase, and the uncertainty of calculated derived values (such as heat capacities and the speed of sound) is likely to exceed the uncertainties of corresponding experimental results, even if the p - ρ - T data are represented accurately. Highly accurate equations of state are thus simultaneously fit to multiple thermodynamic properties.

Early efforts in the development of multiproperty fitting techniques include those of Bender (3), Wagner (4), and McCarty (5). These and other researchers developed algorithms which could be used to fit equations of state simultaneously to p - ρ - T and phase-equilibrium data. The theoretical foundation for the minimization of the sums of squares which include different types of residuals was extended by Ahrendts and Baehr (6).

In modern equations of state, data which are used to develop equations of state usually include p - ρ - T data, thermal phase-equilibrium data (p_σ , ρ' , and ρ''), isobaric heat capacities at gaseous and supercritical states, isochoric heat capacities at liquid and liquid-like supercritical states, speeds of sound, and values of the second and third virial coefficients. However, data for other measured properties may be considered as well. There are few restrictions with regard to the diversity of multiproperty fits.

18.3.3 Constraints

The equation of state may be constrained to exactly represent specific properties at the critical point or elsewhere if such properties are known to sufficient accuracy. If this is appropriate, the final coefficients for the equation of state are determined by a weighted least-squares fit constrained to the critical point data or to other appropriate values using the method of "Lagrangian Multipliers" which was first applied to equations of state by Hust and McCarty (7). Typical critical-point constraints are listed in Table 18.1.

18.3.4 Optimizing the Functional Form of Equations of State

Pressure-explicit empirical equations of state are typically written in reduced form as

$$\frac{P}{\rho RT} = 1 + \sum_{I_{\text{pol}}} n_i \delta^{d_i} \tau^{t_i} + \sum_{I_{\text{exp}}} n_i \delta^{d_i} \tau^{t_i} \exp(-\delta^2) \quad (18.7)$$

with the inverse reduced temperature $\tau = T_c / T$ and the reduced density $\delta = \rho / \rho_c$. The fundamental form in terms of the reduced Helmholtz energy is

Table 18.1 Typical constraints imposed on the equation of state.

Constraint	Numerical Value
Pressure at the critical point	p_c
Density at the critical point	ρ_c
Temperature at the critical point	T_c
Isochore derivative at the critical point	$(\partial p / \partial T)_{\rho_c} = dp/dT _{\sigma}^*$
First derivative of pressure with respect to density at the critical point	$(\partial p / \partial \rho)_{T_c} = 0$
Second and subsequent derivatives of pressure with respect to density at the critical point	$(\partial^2 p / \partial \rho^2)_{T_c} = (\partial^3 p / \partial \rho^3)_{T_c} = 0$

* from the vapor-pressure equation at the critical point

$$\frac{a(T, \rho)}{RT} = \alpha(\tau, \delta) = \alpha^o(\tau, \delta) + \sum_{I_{\text{pol}}} n_i \delta^{d_i} \tau^{t_i} + \sum_{I_{\text{exp}}} n_i \delta^{d_i} \tau^{t_i} \exp(-\delta^{p_i}) + \sum_{I_{\text{crit}}} n_i f_{\text{crit}}(\tau, \delta, \bar{x}_i) \quad (18.8)$$

where the f_{crit} are arbitrary functional forms which are used in some highly accurate equations of state to improve the representation of properties in the critical region and which depend on a vector \bar{x}_i of internal parameters.

The fitting algorithms which were discussed in Sections 18.3.1 to 18.3.3 address only the values of the coefficients n_i in the equations given above. The exponents d_i , t_i , and p_i , the numbers of terms I_{pol} and I_{exp} , and where applicable, I_{crit} , and the vectors \bar{x}_i , are referred to as the "functional form" of the equation of state. This functional form has been chosen based on the experience of the correlator by trial and error strategies. However, the increase in the accuracy of reference equations of state which has been observed over the last two decades was closely related to the development of increasingly powerful optimization algorithms, *e.g.* (8-11), which optimize the functional form of empirical equations of state based on objective statistical criteria. Although these algorithms are very different in detail, the basic idea is same: The user defines a general set of terms which are considered as essentially suitable as terms of an equation of state. Depending on the optimization algorithm used, the number of terms (based on combinations of the "internal parameters" d_i , t_i , and p_i , or of parameter sets \bar{x}_i) in this so called "bank of terms" may vary between 100 and 1000. The optimization algorithm is then used to select the combination of terms out of the bank of terms which yields the smallest sum of squares and thus the best description of the given problem. With the given demands on accuracy and the accuracy of the available experimental data, the number of terms in the optimized equation of state usually varies between 10 and 40, where the optimum number of terms is determined by statistical criteria in most algorithms. The demands on the performance of the optimization algorithm increase with the number of terms in the bank of terms and in the optimized equation, since the number of possible combinations of terms increases rapidly with both values. Optimization algorithms are still being developed, focusing on slightly different methods and goals (12-15).

18.4 PRESSURE-EXPLICIT EQUATIONS OF STATE

Although modern empirical equations of state are usually formulated in terms of the reduced Helmholtz energy, perhaps the most common form of multiparameter equations of state in technical applications is still the pressure explicit form. The discussion that follows highlights several practical forms of multiparameter pressure-explicit equations of state and indicates applications for each.

18.4.1 The Benedict-Webb-Rubin Equation of State

An equation of state that can be extended to reasonably high densities was developed by Benedict *et al.* in 1940 (16). The Benedict-Webb-Rubin (BWR) equation of state is given as

$$p = \rho RT + \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right) \rho^2 + (bRT - a) \rho^3 + a\alpha \rho^6 + \left(\frac{c\rho^3}{T^2} \right) (1 + \gamma \rho^2) \exp(-\gamma \rho^2) \quad (18.9)$$

This equation has eight empirical constants. Values for these constants were reported by Benedict *et al.* (17) for 12 hydrocarbons. An extensive compilation of constants for the BWR equation of state was published by Cooper and Goldfrank (18) in 1967. This equation has been used as the basis for many equations of state which are characterized as modified Benedict-Webb-Rubin equations of state.

In 1962, Strobridge (19) extended the BWR equation of state using the form

$$p = \rho RT + \left(n_1 RT + n_2 + \frac{n_3}{T} + \frac{n_4}{T^2} + \frac{n_5}{T^4} \right) \rho^2 + (n_6 RT + n_7) \rho^3 + n_8 T \rho^4 \\ + \rho^3 \left(\frac{n_9}{T^2} + \frac{n_{10}}{T^3} + \frac{n_{11}}{T^4} \right) \exp(-n_{16} \rho^2) + \rho^5 \left(\frac{n_{12}}{T^2} + \frac{n_{13}}{T^3} + \frac{n_{14}}{T^4} \right) \exp(-n_{16} \rho^2) + n_{15} \rho^6 \quad (18.10)$$

and in 1973, Starling (20) published a further well known modification of the Benedict-Webb-Rubin equation with 11 adjustable coefficients.

The Benedict-Webb-Rubin equation and its simple modifications yield sufficiently accurate results for typical technical applications in the gas phase and at supercritical states with low and medium densities. However, results for caloric properties at liquid or liquid-like supercritical states may be in error by more than $\pm 10\%$. These simple equations are unsuitable when accurate data are required for scientific or advanced technical applications.

18.4.2 The Martin-Hou Equation of State

Martin and Hou (21) developed an equation of state that has been used to correlate the thermodynamic properties of many fluids with particular applications to halocarbon refrigerants. The general form of the Martin-Hou equation of state is

$$p = \frac{RT}{v-b} + \sum_{i=2}^5 \frac{A_i + B_i T + C_i e^{-\gamma}}{(v-b)^i} \quad (18.11)$$

where $\gamma = \kappa T / T_c$. The constants A_i , B_i , C_i , b , and κ are determined by fitting experimental data. Many of the Martin-Hou equations of state developed for the refrigerants include an additional term,

$$p = \frac{RT}{v-b} + \sum_{i=2}^5 \frac{A_i + B_i T + C_i e^{-\gamma}}{(v-b)^i} + \frac{A_6 + B_6 T + C_6 e^{-\gamma}}{e^{uv}(1 + C' e^{uv})} \quad (18.12)$$

where A_6 , B_6 , C_6 , C' , and u are additional fluid-dependent constants. With regard to performance, the Martin-Hou equation is comparable to the Benedict-Webb-Rubin equation and its simple modifications.

18.4.3 The Bender Equation of State

Bender (3,22) developed an equation of state using a modified Benedict-Webb-Rubin form. The Bender equation of state is given as

$$p = \rho T \left[R + B\rho + C\rho^2 + D\rho^3 + E\rho^4 + F\rho^5 + (G + H\rho^2)\rho^2 \exp(-a_{20}\rho^2) \right] \quad (18.13)$$

where the B , C , D , E , F , G , H are temperature polynomials which involve a total of 19 adjustable coefficients. Bender published coefficients for several cryogenic fluids including argon, nitrogen, oxygen, carbon dioxide, and methane. The Bender equation was used by Maurer and coworkers during the 80's to describe a broad variety of technically relevant substances. The theses of Polt (23) and Platzner (24) contain Bender equations for more than 50 substances which have only been partly published internationally.

The Bender equation was one of the first modifications of the Benedict-Webb-Rubin equation which was designed to describe vapor-liquid phase equilibria properly as well as caloric properties in the liquid phase with results which are sufficiently accurate for common technical applications. However, numerical stability problems often lead to significantly erroneous results for substances with limited data sets.

18.4.4 The Jacobsen-Stewart Equation of State

In 1973, Jacobsen and Stewart (25) developed the most advanced form of a modified Benedict-Webb-Rubin equation of state which became known as *the mBWR equation*. This equation of state is given by

$$p = \sum_{n=1}^9 a_n \rho^n + \exp(-\gamma \rho^2) \sum_{n=10}^{15} a_n \rho^{2n-17} \quad (18.14)$$

where $\gamma = 1/\rho_c^2$. There are 32 constants in this equation of state. The a_n polynomials are:

$$\begin{aligned}
a_1 &= RT \\
a_2 &= b_1 T + b_2 T^{1/2} + b_3 + b_4 T^{-1} + b_5 T^{-2} \\
a_3 &= b_6 T + b_7 + b_8 T^{-1} + b_9 T^{-2} \\
a_4 &= b_{10} T + b_{11} + b_{12} T^{-1} \\
a_5 &= b_{13} \\
a_6 &= b_{14} T^{-1} + b_{15} T^{-2} \\
a_7 &= b_{16} T^{-1} \\
a_8 &= b_{17} T^{-1} + b_{18} T^{-2} \\
a_9 &= b_{19} T^{-2} \\
a_{10} &= b_{20} T^{-2} + b_{21} T^{-3} \\
a_{11} &= b_{22} T^{-2} + b_{23} T^{-4} \\
a_{12} &= b_{24} T^{-2} + b_{25} T^{-3} \\
a_{13} &= b_{26} T^{-2} + b_{27} T^{-4} \\
a_{14} &= b_{28} T^{-2} + b_{29} T^{-3} \\
a_{15} &= b_{30} T^{-2} + b_{31} T^{-3} + b_{32} T^{-4}
\end{aligned} \tag{18.15}$$

In the original work of Jacobsen and Stewart (25), this functional form was used in the development of an equation of state for nitrogen. Since then, this form has been used by many researchers for other fluids. The mBWR equation is sufficiently accurate to satisfy advanced technical and common scientific demands on accuracy and has been used as reference equations for the properties of a variety of fluids, including refrigerants and cryogenics.

18.5 THERMODYNAMIC PROPERTIES FROM PRESSURE-EXPLICIT EQUATIONS OF STATE

The values of entropy, enthalpy, internal energy, and heat capacity at various state points are calculated using the pressure explicit equation of state and an ancillary ideal-gas heat capacity equation. The vapor-pressure equation and the melting-curve equation are used to identify the temperatures of the phase changes from liquid to vapor and solid to liquid, respectively. Integral representations for properties are continuously integrated through the two-phase region to calculate properties in the liquid. This procedure is valid if the equation of state was developed using procedures to include the conditions for two-phase equilibrium in the least-squares determination of the coefficients in the equation of state. The relations for the calculation of thermodynamic properties are summarized below. Functions for the integrals and derivatives of the equation of state required to perform these calculations are based upon the specific pressure-explicit equation of state used.

The entropy of any thermodynamic state is calculated from

$$s(T, \rho) = s_{T_0}^0 + \int_{T_0}^T \left(\frac{c_p^0}{T} \right) dT - R \ln(RT\rho) + \int_0^{\rho} \left[\frac{R}{\rho} - \left(\frac{1}{\rho^2} \right) \left(\frac{\partial p}{\partial T} \right)_{\rho} \right] d\rho \tag{18.16}$$

An ancillary equation is used to evaluate the ideal-gas specific heat, c_p^0 . The reference entropy of the ideal gas at T_0 and p_0 is taken from a suitable source for the fluid under investigation. The enthalpy of any state may be calculated from

$$h(T, \rho) = h_{T_0}^0 + T \int_0^{\rho} \left[\left(\frac{p}{T\rho^2} \right) - \left(\frac{1}{\rho^2} \right) \left(\frac{\partial p}{\partial T} \right)_{\rho} \right] d\rho + \left(\frac{p - \rho RT}{\rho} \right) + \int_{T_0}^T c_p^0 dT \tag{18.17}$$

It is convenient to replace the first integral term in this equation with

$$T \int_0^p \left[\left(\frac{p}{T\rho^2} \right) - \left(\frac{1}{\rho^2} \right) \left(\frac{\partial p}{\partial T} \right)_\rho \right] d\rho = T \int_0^p \left[\left(\frac{R}{\rho} \right) - \left(\frac{1}{\rho^2} \right) \left(\frac{\partial p}{\partial T} \right)_\rho \right] d\rho + \int_0^p \left[\left(\frac{p}{\rho^2} \right) - \left(\frac{RT}{\rho} \right) \right] d\rho \quad (18.18)$$

The resulting expression for enthalpy is

$$\begin{aligned} h(T, \rho) = h_{T_0}^0 + T \int_0^p \left[\left(\frac{R}{\rho} \right) - \left(\frac{1}{\rho^2} \right) \left(\frac{\partial p}{\partial T} \right)_\rho \right] d\rho \\ + \int_0^p \left[\left(\frac{p}{\rho^2} \right) - \left(\frac{RT}{\rho} \right) \right] d\rho + \left(\frac{p}{\rho} - RT \right) + \int_{T_0}^T c_p^0 dT \end{aligned} \quad (18.19)$$

The reference enthalpy of the ideal gas at T_0 and p_0 is taken from a separate source. The internal energy of a fluid state is calculated from

$$u(T, \rho) = h(T, \rho) - \frac{p}{\rho} \quad (18.20)$$

The specific heat at constant volume, c_v , is calculated using the relation

$$c_v(T, \rho) = (c_p^0 - R) - \int_0^p \left[\left(\frac{T}{\rho^2} \right) \left(\frac{\partial^2 p}{\partial T^2} \right)_\rho \right] d\rho \quad (18.21)$$

The specific heat at constant pressure, c_p , is calculated using the relation

$$c_p(T, \rho) = c_v(T, \rho) + \left[\left(\frac{T}{\rho^2} \right) \left(\frac{\partial p}{\partial T} \right)_\rho^2 \left(\frac{\partial \rho}{\partial p} \right)_T \right] \quad (18.22)$$

18.6 FUNDAMENTAL EQUATIONS

Fundamental equations contain calorimetric and reference state information so that absolute values of specified properties may be calculated directly by differentiation without additional information. For simple pure-fluid systems in equilibrium with their environments, a number of equivalent fundamental relations may be stated. The four typical forms are given as

$$u = u(s, v) \quad (18.23)$$

$$h = h(s, p) \quad (18.24)$$

$$a = a(T, v) \quad (18.25)$$

$$g = g(T, p) \quad (18.26)$$

Equations (18.23) and (18.24) are not used for correlation work because the independent variable s is not measurable. Equation (18.26) can only be used to represent the liquid surface or the vapor surface, but not both due to the discontinuity in slope at the phase boundaries in the Gibbs energy. Two independent formulations would be required for the vapor and liquid phases, and matching these formulations at supercritical conditions would be nearly impossible. Thus, the formulation for the Helmholtz energy, Equation (18.25), with independent variables T and v (or ρ), or their nondimensional equivalents, δ and τ , are the only fundamental relations suitable for the development of equations of state which describe the whole fluid region.

The following sections present descriptions of Helmholtz energy equations of state used to represent the thermodynamic properties of a number of fluids over wide ranges of temperatures and pressures. Although the selection of examples is admittedly arbitrary, those given here are selected to illustrate both the theoretical basis and the empirical nature of each.

18.6.1 The Equation of Keenan, Keyes, Hill, and Moore

As early as 1940, Benedict, Webb, and Rubin published their formulation both in terms of pressure and in the residual Helmholtz energy. However, the formulation in pressure was considered the original formulation and the Helmholtz-energy formulation was rarely used since the ideal-gas contribution was missing. The first equation of state which was formulated exclusively in terms of the Helmholtz energy was published in 1969 by Keenan, Keyes, Hill, and Moore (26) for water and steam. The equation is given as

$$a = a_0(T) + RT \ln \rho + RT \rho Q(\rho, \tau) \quad (18.27)$$

where $\tau = 1000 \text{ K}/T$. In this formulation for steam, ρ is the density in $\text{g}\cdot\text{cm}^{-3}$. The function $a_0(T)$ represents the ideal-gas behavior of the fluid and is given by

$$a_0(T) = \sum_{i=1}^6 \frac{C_i}{\tau^{i-1}} + C_7 \ln T + \frac{C_8 \ln T}{\tau} \quad (18.28)$$

The empirical function $Q(\rho, \tau)$ describes the residual contribution to the Helmholtz energy and is expressed as

$$Q(\rho, \tau) = (\tau - \tau_c) \sum_{j=1}^7 (\tau - \tau_{aj})^{j-2} \left[\sum_{i=1}^8 A_{ij} (\rho - \rho_{aj})^{i-1} + e^{-E\rho} \sum_{i=9}^{10} A_{ij} \rho^{i-9} \right] \quad (18.29)$$

Today, this equation of state with fifty coefficients, A_{ij} , in the residual part of the Helmholtz energy is interesting only for historical aspects.

18.6.2 The Equation of Pollak

Pollak (27) developed an equation of state for water (27) in 1975 which is expressed as

$$\frac{a(\rho, T)}{RT} = \alpha(\delta, \tau) = \alpha^0(\tau) + \ln \frac{\delta}{\delta_t} + \alpha^r(\delta, \tau) \quad (18.30)$$

where $\delta = \rho/\rho^+$, $\tau = T/T_t$, T_t is the triple-point temperature, δ_t is 0.99977602, and ρ^+ is $1 \text{ g}\cdot\text{cm}^{-3}$. The term $\alpha^0(\tau)$ is a simple polynomial with 10 coefficients representing the ideal gas contribution to the dimensionless Helmholtz energy and $\alpha^r(\delta, \tau)$ is the empirical correlation for the residual Helmholtz energy. The function $\alpha^r(\delta, \tau)$ is given by

$$\alpha^r(\delta, \tau) = \sum_{i=1}^{24} a_i \delta^i \tau^{t_i} + \exp(-A_i \delta^2) \sum_{i=25}^{40} a_i \delta^i \tau^{t_i} \quad (18.31)$$

This 40 coefficient equation used terms for the first time which could not have been used in a pressure-explicit equation since they could not be integrated analytically. This advantage increased the flexibility and the accuracy in representing thermodynamic properties while formulating Helmholtz-energy equations of state.

18.6.3 The Equations of Haar and Gallagher and Haar, Gallagher, and Kell

In 1978, Haar and Gallagher (28) developed an equation of state for ammonia and in 1984 Haar, Gallagher and Kell (29) published an equation of state for water. Both equations became accepted standards, and although they have been superseded by more recent formulations by Baehr and Tillner-Roth (30) for ammonia and Wagner and Pruss (31,32) for water, they are still frequently used in industrial applications.

The ammonia equation by Haar and Gallagher is given as

$$a(\rho, T) = a^0(T) + a^r(\rho, T) \quad (18.32)$$

where $a^0(T)$ is the contribution of the ideal gas and $a^r(\rho, T)$ is the residual contribution. The ideal-gas contribution is given as

$$a^0(T) = RT \left[a_1 \ln T + \sum_{i=2}^{11} a_i T^{i-3} - 1 + \ln(4.818T) \right] \quad (18.33)$$

The residual is given by

$$a^r(\rho, T) = RT \left[\ln(\rho) + \rho \left(\sum_{i=1}^9 \sum_{j=1}^6 a_{ij} \rho^{i-1} (\tau - \tau_c)^{j-1} \right) \right] \quad (18.34)$$

where $\tau = 500 \text{ K}/T$ and $\tau_c = 1.2333498$.

The equation of state for water is composed of a base function, a residual component, and the ideal gas contribution,

$$a(\rho, T) = a^0(T) + a_{\text{base}}(\rho, T) + a^r(\rho, T) \quad (18.35)$$

The ideal-gas contribution to the Helmholtz energy is given as

$$a^0(T) = -RT \left[1 + \left(\frac{C_1}{T_R} + C_2 \right) \ln T_R + \sum_{i=3}^{18} C_i T_R^{i-6} \right] \quad (18.36)$$

where $T_R = T/100$ K.

The base function is used to represent the dilute-gas region and is derived from the Ursell-Mayer virial theory. It is given as

$$a_{\text{base}}(\rho, T) = RT \left[-\ln(1-y) - \frac{\beta-1}{1-y} + \frac{\alpha+\beta+1}{2(1-y)^2} + 4y \left(\frac{B}{b} - \gamma \right) - \frac{\alpha-\beta+3}{2} + \ln \frac{\rho RT}{p_0} \right] \quad (18.37)$$

where y is $b\rho/4$, and α , β , and γ are constants. B and b are temperature-dependent molecular parameters which contain eight adjustable coefficients. The residual part consists of 40 terms. The functional form is

$$a^r(\rho, T) = \sum_{i=1}^{36} \frac{a_i}{k_i} \left(\frac{T_0}{T} \right)^{l_i} (1 - e^{-\rho})^{k_i} + \sum_{i=37}^{40} a_i \delta_i^{l_i} \exp(-\alpha_i \delta_i^{k_i} - \beta_i \tau_i^2) \quad (18.38)$$

where the coefficients and exponents, a_i , k_i , and l_i , are determined by fitting experimental data. In this equation, δ and τ are functions of density and temperature given by

$$\delta_i = \frac{\rho - \rho_i}{\rho_i} \quad (18.39)$$

$$\tau_i = \frac{T - T_i}{T_i} \quad (18.40)$$

where ρ_i and T_i are specified density and temperature values.

18.6.4 The Equation of Schmidt and Wagner

In the mid 80's, Schmidt and Wagner (33) and Jacobsen *et al.* (34) developed equations of state which can be regarded as the origin of most of our recent reference equations of state. Optimization algorithms (see Section 18.3.4) were used for the first time to determine the functional form of equations of state.

In the equation of Schmidt and Wagner (33), the reduced Helmholtz energy is given as

$$\frac{a(\rho, T)}{RT} = \alpha(\delta, \tau) = \alpha^0(\delta, \tau) + \alpha^r(\delta, \tau) \quad (18.41)$$

where $\tau = T_c/T$, $\delta = \rho/\rho_c$, T_c is the critical temperature, and ρ_c is the critical density. In general, the ideal-gas contribution is given by

$$\alpha^0(\delta, \tau) = \frac{h_0^0 \tau}{RT_c} - \frac{s_0^0}{R} - 1 + \ln \frac{\delta \tau_0}{\delta_0 \tau} - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau^2} d\tau + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau} d\tau \quad (18.42)$$

For oxygen, this equation results in

$$\begin{aligned} \alpha^0(\delta, \tau) = & k_1 \tau^{1.5} + k_2 \tau^{-2} + k_3 \ln \tau + k_4 \tau + k_5 \ln[\exp(k_7 \tau) - 1] \\ & + k_6 \ln[1 + \frac{2}{3} \exp(-k_8 \tau)] + k_9 + \frac{h^0(\tau_0)}{RT} - \frac{s^0(\delta_0, \tau_0)}{R} + \ln \frac{\delta}{\delta_0} \end{aligned} \quad (18.43)$$

where $\tau_0 = T_c/T_0$, $\delta_0 = p_0/(RT_0 \rho_c)$, $T_0 = 298.15$ K and $p_0 = 0.101325$ MPa.

The evolutionary optimization algorithm by Ewers and Wagner (10) was used to establish the functional form of the final equation based on the "bank of terms" created from the equation

$$\alpha^r(\delta, \tau) = \sum_{i=1}^9 \sum_{j=-1}^{12} a_{ij} \delta^i \tau^{j/2} + \exp(-\delta^2) \sum_{i=0}^{10} \sum_{j=4}^{17} a_{ij} \delta^i \tau^{j/2} + \exp(-\delta^4) \sum_{i=2}^5 \sum_{j=10}^{23} a_{ij} \delta^i \tau^j \quad (18.44)$$

containing 336 terms. The final optimized equation reads

$$\alpha^r(\delta, \tau) = \sum_{i=1}^{13} a_i \delta^{r_i} \tau^{s_i} + \exp(-\delta^2) \sum_{i=14}^{24} a_i \delta^{r_i} \tau^{s_i} + \exp(-\delta^4) \sum_{i=25}^{32} a_i \delta^{r_i} \tau^{s_i} \quad (18.45)$$

This equation introduced exponential terms of the type $\exp(-\delta^4)$ which resulted in substantial improvements with regard to the representation of properties in the critical region.

18.6.5 The Equation of Jacobsen, Stewart, Jahangiri, and Penoncello

Jacobsen *et al.* (34) developed an equation of state in terms of the reduced Helmholtz energy with the same format as defined by Equations (18.41) and (18.42), although a different bank of terms was formulated for the residual part of the Helmholtz energy and is given by

$$\alpha^r(\delta, \tau) = \sum_{k=1}^m a_k \delta^{i_k} \tau^{j_k} \exp(-\gamma \delta^{l_k}) \quad (18.46)$$

where $\gamma = 0$ for terms with $l_k = 0$ and $\gamma = 1$ for terms where $l_k \neq 0$. The i_k and l_k are positive integers and the j_k are real numbers (positive or negative). The number of terms in this equation was originally restricted to 100 for efficient use with a modified form of the stepwise regression analysis (8) which is a purely deterministic optimization algorithm. However, by preselecting the terms to be used in the bank of terms, they obtained high flexibility with regard to the functional form of the resulting equation of state. In addition, the equation used exponential functions with density exponents l_k other than 2 or 4.

The terms in the final equation of state are a substance specific subset of the terms in Equation (18.46) which was originally used to formulate the thermodynamic properties of air, nitrogen, argon, and oxygen.

18.6.6 Recent Equations of State

In combination with a suitable optimization algorithm, the functional forms introduced in the banks of terms by Schmidt and Wagner (33) and Jacobsen *et al.* (34) are sufficient to match the uncertainty of very accurate experimental data with an acceptable number of terms. In general, more complex functional forms are required only to accurately describe the properties in the critical region. As an example of the performance of a recent equation of state, Figure 18.1 shows deviations between accurate experimental data for the density of 1,1,1,2-tetrafluoroethane (HFC-134a) and values calculated from the equation of Tillner-Roth and Baehr (35). The residual part of this equation is

$$\alpha^r(\delta, \tau) = \sum_{i=1}^8 a_k \delta^{d_i} \tau^{t_i} + \sum_{i=9}^{21} a_k \delta^{d_i} \tau^{t_i} \exp(-\delta^{p_i}) \quad (18.47)$$

where the temperature exponents are multiples of 0.5 and the density exponents in the exponential function range from 1 to 4.

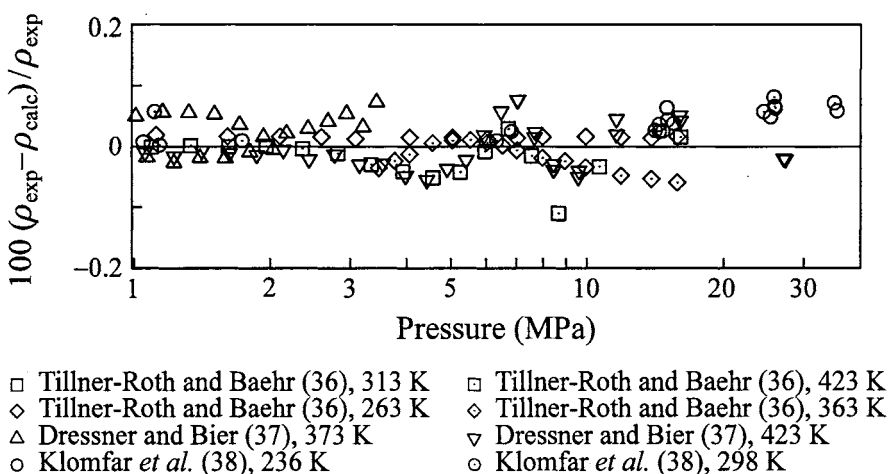


Figure 18.1 Deviation plot comparing density values calculated from the equation of state of Tillner-Roth and Baehr (35) for HFC-134a to experimental P - ρ - T data.

A larger number of terms is necessary when even higher accuracies are required for certain reference substances. With smaller temperature increments in the bank of terms, the increase in the number of terms in the equation of state can be limited to reasonable values. However,

the demands on the performance of optimization algorithms increase with additional terms in both the equation of state and in the bank of terms. Figure 18.2 shows a comparison between experimental results for the density of nitrogen and values calculated from the reference equation by Span *et al.* (39). The residual part of this equation is

$$\alpha^r(\delta, \tau) = \sum_{i=1}^6 a_k \delta^{d_i} \tau^{t_i} + \sum_{i=7}^{32} a_k \delta^{d_i} \tau^{t_i} \exp(-\delta^{p_i}) + \sum_{i=33}^{36} a_k \delta^{d_i} \tau^{t_i} \exp(-\varphi_i(\delta-1)^2 - \beta_i(\tau-\gamma_i)^2) \quad (18.48)$$

where the temperature exponents are multiples of 0.125 and the density exponents in the exponential function range from 1 to 4. The functional form of this equation was selected from a bank of terms which contained a total of 838 terms.

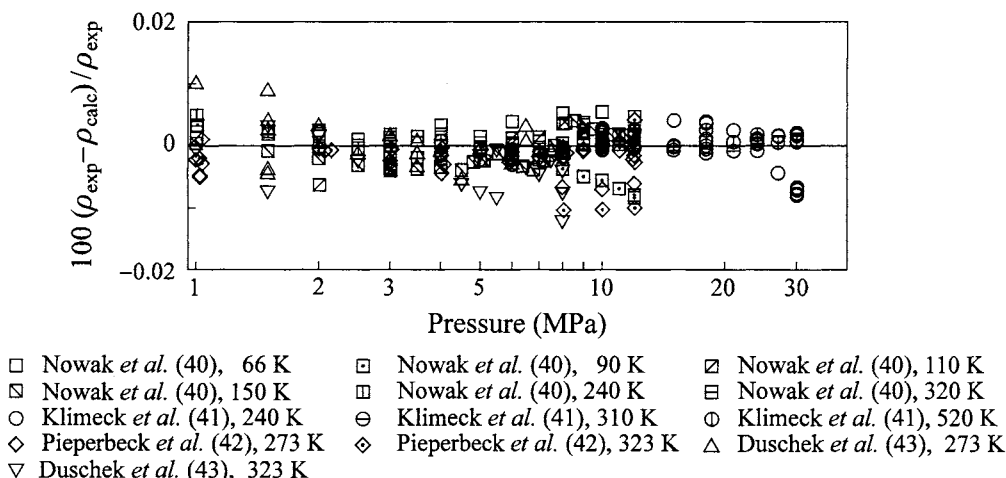


Figure 18.2 Deviation plot comparing density values calculated from the equation of state of Span *et al.* (39) for nitrogen to experimental P - ρ - T data.

The terms in the third sum in Equation (18.48) correspond to so called "modified Gaussian bell shaped terms" which were introduced by Setzmann and Wagner (44) to improve the description of properties in the critical region. In addition to methane (44) and nitrogen (39), such terms were used in the recent equations for carbon dioxide (45), water (31,32), argon (46) and ethylene (47). The equations for carbon dioxide (45) and water (31,32) additionally include "nonanalytic terms" which improve the description of isochoric heat capacities and speeds of sound in the critical region. The equation for the residual part of the Helmholtz energy of carbon dioxide is

$$\alpha^r(\delta, \tau) = \sum_{i=1}^7 a_k \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{34} a_k \delta^{d_i} \tau^{t_i} \exp(-\delta^{p_i}) + \sum_{i=35}^{39} a_k \delta^{d_i} \tau^{t_i} \exp(-\varphi_i(\delta-1)^2 - \beta_i(\tau-\gamma_i)^2) + \sum_{i=40}^{42} a_k \delta \Delta^{b_i} \exp(-C_i(\delta-1)^2 - D_i(\tau-1)^2) \quad (18.49)$$

with $\Delta = \left\{ (1-\tau) + A_i \left[(\delta-1)^2 \right]^{1/(2\beta_i)} \right\}^2 + B_i \left[(\delta-1)^2 \right]^{c_i}$. In this equation, the nonanalytic terms correspond to the fourth sum. Figure 18.3 shows typical plots of the isochoric heat capacity in the critical region as they result from equations which use only polynomial and exponential terms (A), which additionally use modified Gaussian bell shaped terms (B), and which include both modified Gaussian bell shaped and nonanalytic terms (C). Curve D corresponds to values calculated from a crossover formulation (see Chapter 11) which yields exactly the theoretically predicted limiting behavior at the critical point. Even though equations with nonanalytic terms yield a diverging isochoric heat capacity and a vanishing speed of sound at the critical point, they do not fulfill all theoretical expectations (45). Work on further improvements of empirical critical region terms continues in different groups around the world.

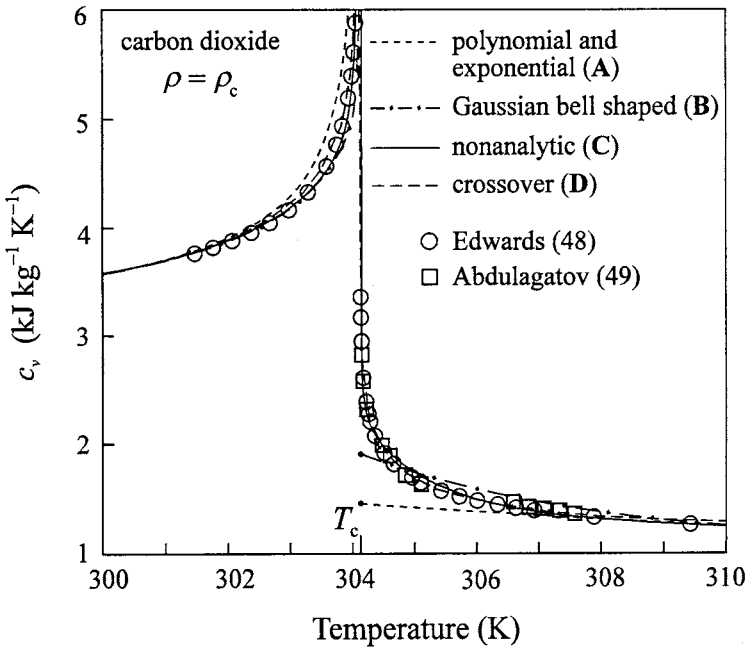


Figure 18.3 Values calculated for the isochoric heat capacity on the critical isochore of carbon dioxide calculated from different types of equations of state.

18.6.7 Transition (or Unified) Equations

Rather than improving the performance of empirical equations of state by introducing special critical region terms, one may combine them with a scaled equation of state which yields the theoretically expected limiting behavior at the critical point (but not necessarily the best possible description of accurate experimental data). The best example of such an equation is the one for water developed by Hill (50) which allows a smooth transition in calculated properties from the singular critical-region functions to the analytic ones for the classical wide-range behavior without discontinuities or oscillations in the functions or their derivatives.

The unified equation of state of Hill (50) is explicit in the Helmholtz energy, given as

$$\bar{\psi} = \bar{\psi}_f + F(\bar{\psi}_n - \bar{\psi}_f) \quad (18.50)$$

in which $\bar{\psi}_f = \bar{\psi}_f(\bar{\rho}, \bar{T})$ is the "far field" function and $\bar{\psi}_n = \bar{\psi}_n(\bar{\rho}, \bar{T})$ is the function "near" the critical point. The "switching" function,

$$F = 1 - \exp(-1/Z) \quad (18.51)$$

is unity at the critical point and is zero everywhere outside the critical region. The far-field equation, $\bar{\psi}_f$, is given by

$$\bar{\psi}_f = \ln \bar{\rho} + \bar{\psi}_o + \bar{\psi}_1(\bar{\rho}, \bar{T}) \quad (18.52)$$

in which the first two terms pertain to the ideal gas. The function $\bar{\psi}_1(\bar{\rho}, \bar{T})$ is written as

$$\bar{\psi}_1 = W_1 + EW_2 + GW_3 + HW_4 \quad (18.53)$$

where W_1 , W_2 , W_3 , and W_4 are empirical correlations involving polynomials in terms of temperature and density as well as exponential functions.

18.7 THERMODYNAMIC PROPERTIES FROM HELMHOLTZ-ENERGY EQUATIONS OF STATE

The following equations give the relations among the common thermodynamic properties including those frequently measured for fluids of engineering importance. These relations are derived from the fundamental equation given as Equation (18.41).

$$p = \rho RT \left(1 + \delta \frac{\partial \alpha^r}{\partial \delta} \right) \quad (18.54)$$

$$\frac{u}{RT} = \tau \left(\frac{\partial \alpha^o}{\partial \tau} + \frac{\partial \alpha^r}{\partial \tau} \right) \quad (18.55)$$

$$\frac{s}{R} = \tau \left(\frac{\partial \alpha^o}{\partial \tau} + \frac{\partial \alpha^r}{\partial \tau} \right) - \alpha^o - \alpha^r \quad (18.56)$$

$$\frac{h}{RT} = \tau \left(\frac{\partial \alpha^0}{\partial \tau} + \frac{\partial \alpha^r}{\partial \tau} \right) + \delta \frac{\partial \alpha^r}{\partial \delta} + 1 \quad (18.57)$$

$$\frac{g}{RT} = 1 + \alpha^0 + \alpha^r + \delta \frac{\partial \alpha^r}{\partial \delta} \quad (18.58)$$

$$\frac{c_v}{R} = -\tau^2 \left(\frac{\partial^2 \alpha^0}{\partial \tau^2} + \frac{\partial^2 \alpha^r}{\partial \tau^2} \right) \quad (18.59)$$

$$\frac{c_p}{R} = \frac{c_v}{R} + \frac{\left[1 + \delta \frac{\partial \alpha^r}{\partial \delta} - \delta \tau \frac{\partial^2 \alpha^r}{\partial \delta \partial \tau} \right]^2}{\left[1 + 2\delta \frac{\partial \alpha^r}{\partial \delta} + \delta^2 \frac{\partial^2 \alpha^r}{\partial \delta^2} \right]} \quad (18.60)$$

$$\frac{w^2 M}{RT} = 1 + 2\delta \frac{\partial \alpha^r}{\partial \delta} + \delta^2 \frac{\partial^2 \alpha^r}{\partial \delta^2} - \frac{\left[1 + \delta \frac{\partial \alpha^r}{\partial \delta} - \delta \tau \frac{\partial^2 \alpha^r}{\partial \delta \partial \tau} \right]^2}{\tau^2 \left[\frac{\partial^2 \alpha^0}{\partial \tau^2} + \frac{\partial^2 \alpha^r}{\partial \tau^2} \right]} \quad (18.61)$$

These relationships are readily used in computer programs for the calculation of thermodynamic properties. Other properties can be calculated by differentiation of the fundamental equation.

18.8 COMPARISONS OF PROPERTY FORMULATIONS

Regardless of whether the property formulation for a particular fluid is explicit in pressure, Helmholtz energy, Gibbs energy, or another property, the user must be given an assessment of its accuracy for practical applications. The quality of a thermodynamic property formulation is best determined by its ability to model the physical behavior of the fluid as represented by the available experimental data. Group statistics or extensive deviation plots are commonly used to show how thermodynamic properties calculated from equations of state compare to experimental data.

The group statistics typically used are based on the percent deviation of a property, $\% \Delta x$,

$$\% \Delta x = 100 \left(\frac{x_{\text{data}} - x_{\text{calc}}}{x_{\text{data}}} \right) \quad (18.62)$$

The statistics used to compare properties calculated from an equation of state to experimental data are summarized below:

$$\text{AAD} = \frac{1}{n} \sum_{i=1}^n |\% \Delta x_i| \quad (18.63)$$

$$\text{BIAS} = \frac{1}{n} \sum_{i=1}^n (\% \Delta x_i) \quad (18.64)$$

$$\text{SDV} = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (\% \Delta x_i - \text{BIAS})^2} \quad (18.65)$$

$$\text{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^n (\% \Delta x_i)^2} \quad (18.66)$$

In these equations, n is the number of data points being considered. Equation (18.63) is the absolute average deviation (AAD) of a data set. High values of the AAD indicate either a systematic or large random difference between the data and the equation of state. The bias (BIAS) value in Equation (18.64) is the average deviation of the data set. Large positive or negative values of the bias indicate systematic differences between the data and the equation of state. SDV from Equation (18.65) is the standard deviation for a data set. This value gives an indication of the systematic or random dispersion of the data set about the BIAS value. Equation (18.66) is the root-mean-square (RMS) value of the deviations. This parameter provides another indication of the systematic or random dispersion of the data from the equation of state. Data sets are accurately represented by an equation of state when all four statistical parameters are near zero. In a practical sense, the values of the parameters should be small.

The typical performance of recent reference equations of state for technically relevant fluids (HFC-134a in Figure 18.1) and, in addition, for scientifically and meteorologically relevant fluids (nitrogen in Figure 18.2) has already been discussed in Section 18.6.6. These figures show a general overview of the deviations between an equation of state and experimental data. Further examples comparing values calculated from the equation of state for HFC-134a by Tillner-Roth and Bachr (35) with selected experimental data are given in Figures 18.4 and 18.5. Data for HFC-134a have been used here for comparisons because they are part of a large, accurate data set for a typical technically relevant fluid which have been measured in the last few years using modern experimental techniques. Figure 18.4 compares calculated values with experimental liquid isochoric heat capacity data of Magee (51), the vapor speed of sound data of Goodwin and Moldover (52), and the liquid speed-of-sound data of Guedes and Zollweg (53). Figure 18.5 compares calculated values using the Maxwell criteria for saturation properties with experimental vapor pressures and liquid and vapor saturated densities. Figure 18.4 shows how detailed comparisons with multiple isochores and isotherms would be made during the development of an equation of state allowing one to identify bad data or systematic problems with the equation. These comparisons should be used in detailed presentations of equations of state. While tedious, these graphical comparisons of calculated properties to measured data values are the most useful illustration of the accuracy of a property formulation.

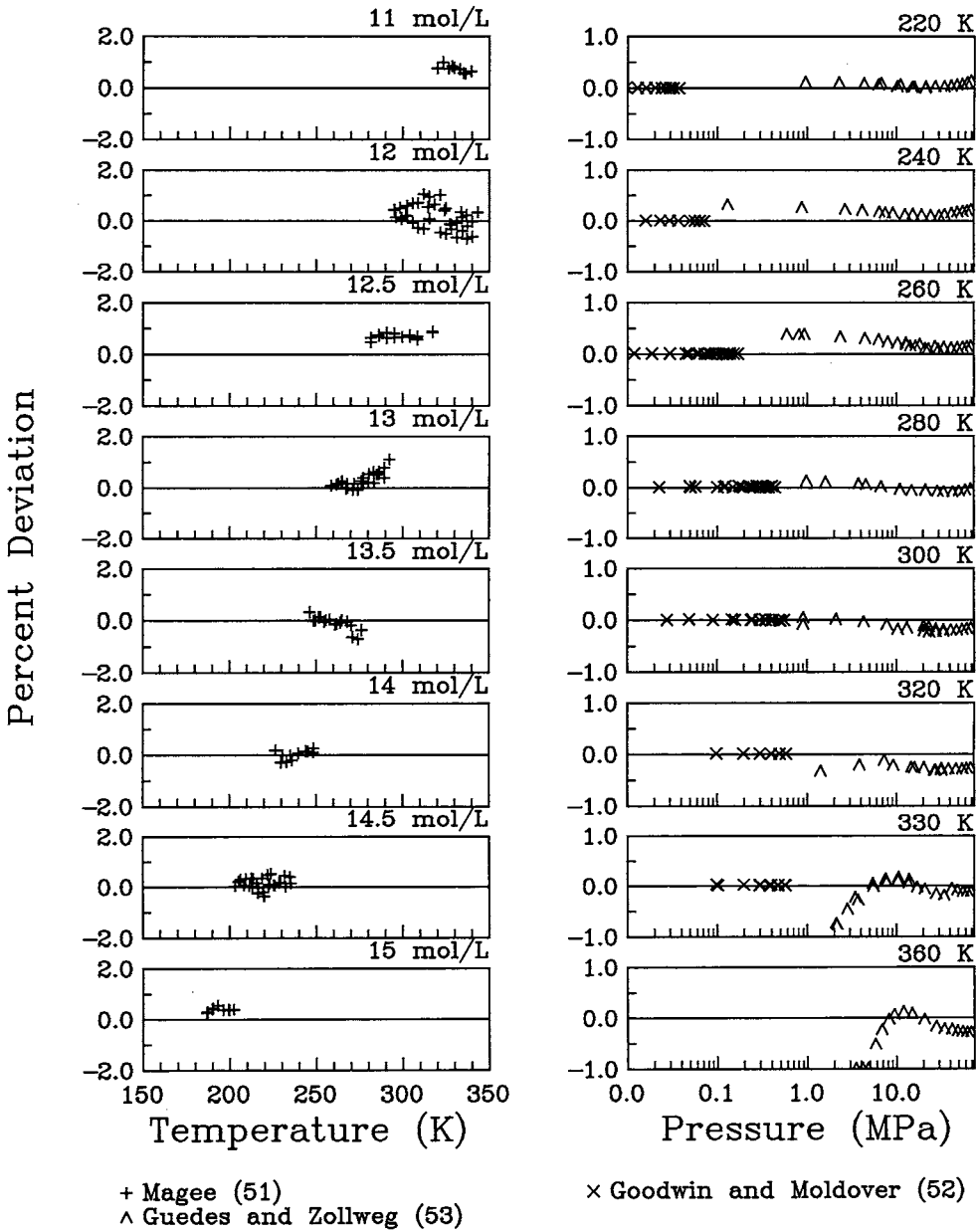


Figure 18.4 Deviation plot comparing isochoric heat capacity (left side) and speed of sound (right side) values calculated from the equation of state of Tillner-Roth and Baehr (35) for HFC-134a to experimental data.

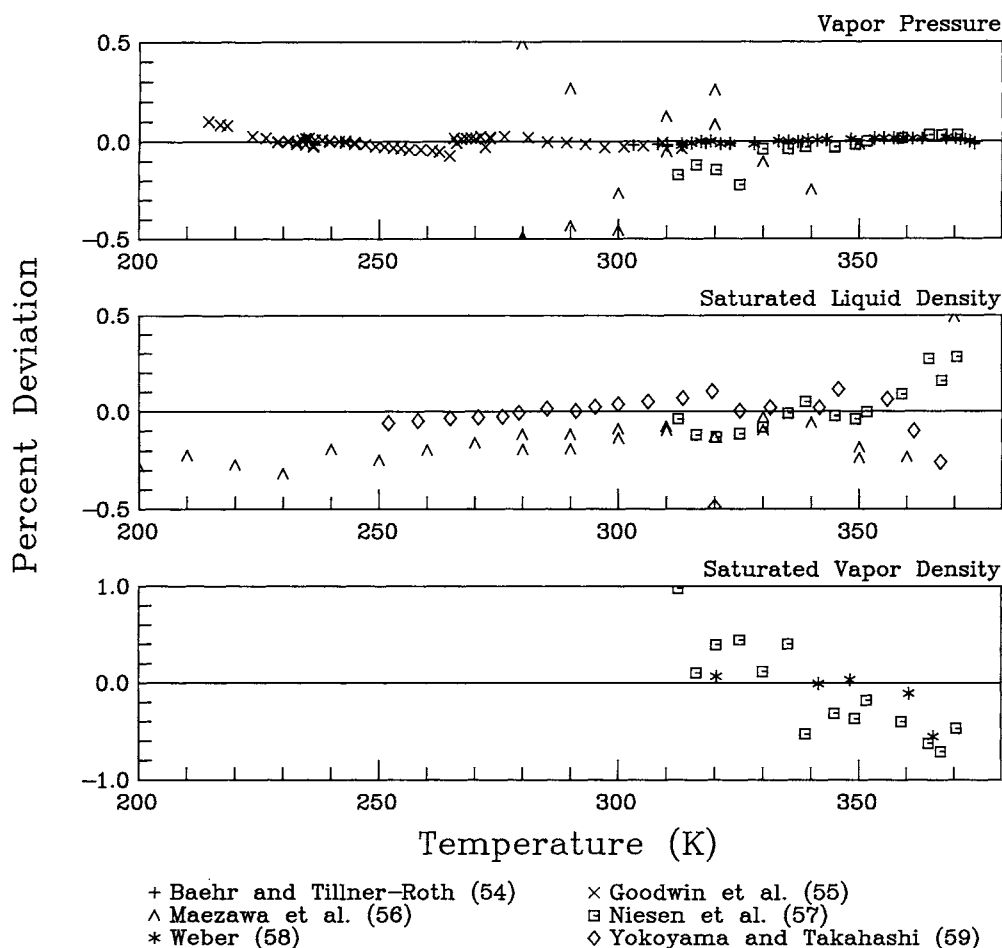


Figure 18.5 Deviation plot comparing saturation property values calculated from the equation of state of Tillner-Roth and Baehr (35) for HFC-134a to experimental data.

Constant property lines calculated from the formulation over wide ranges of temperature and pressure help to examine the qualitative behavior of equations of state particularly in regions which are difficult to describe, such as the critical region or the liquid region at low reduced temperatures. Examples of such graphical representations are given in Figures 18.6 and 18.7 for the formulation for HFC-134a by Tillner-Roth and Baehr (35). In general, calculations of heat capacities, sound speeds, and other derived properties are more sensitive to poor behavior of the equation of state than those of basic properties such as pressure or enthalpy.

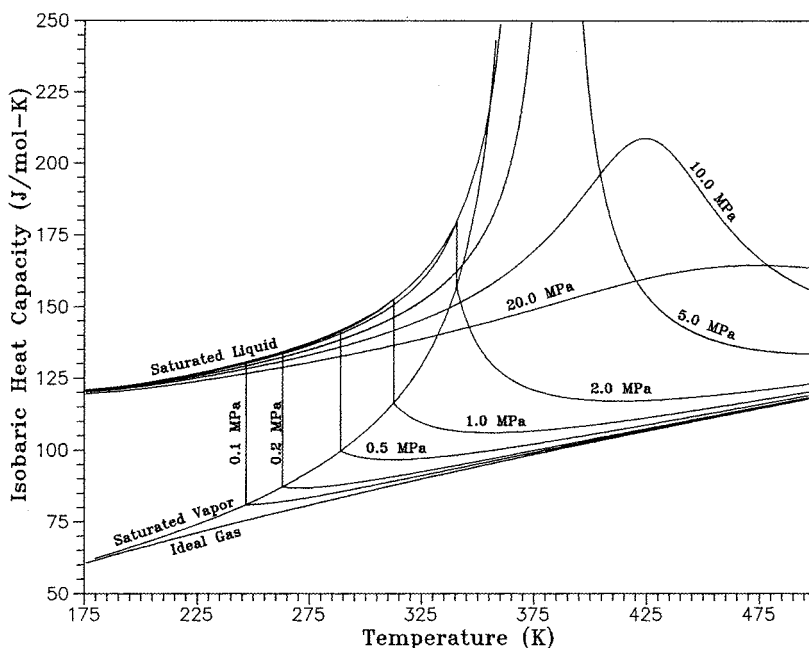


Figure 18.6 Isobaric heat capacities for HFC-134a calculated from the equation of state of Tillner-Roth and Baehr (35).

The extrapolation behavior of empirical multiparameter equations of state has recently been summarized by Span and Wagner (60). Aside from the representation of fugacities at temperatures and pressures which exceed the range of primary data and the representation of shock tube data for the Hugoniot curve at very high temperatures and pressures, an assessment of the extrapolation behavior of an equation of state can be based on "ideal curves" which were first discussed by Brown (61). Figure 18.8 shows plots of these ideal curves as they were calculated from three different generations of reference equations of state for nitrogen. While reference equations of state generally result in reasonable plots for the Boyle, ideal, and Joule-Thomson inversion curves, the prediction of reasonable Joule inversion curves is still a challenging demand. Older equations may result in unreasonable plots even for the first three curves, especially when they are based on limited data sets.

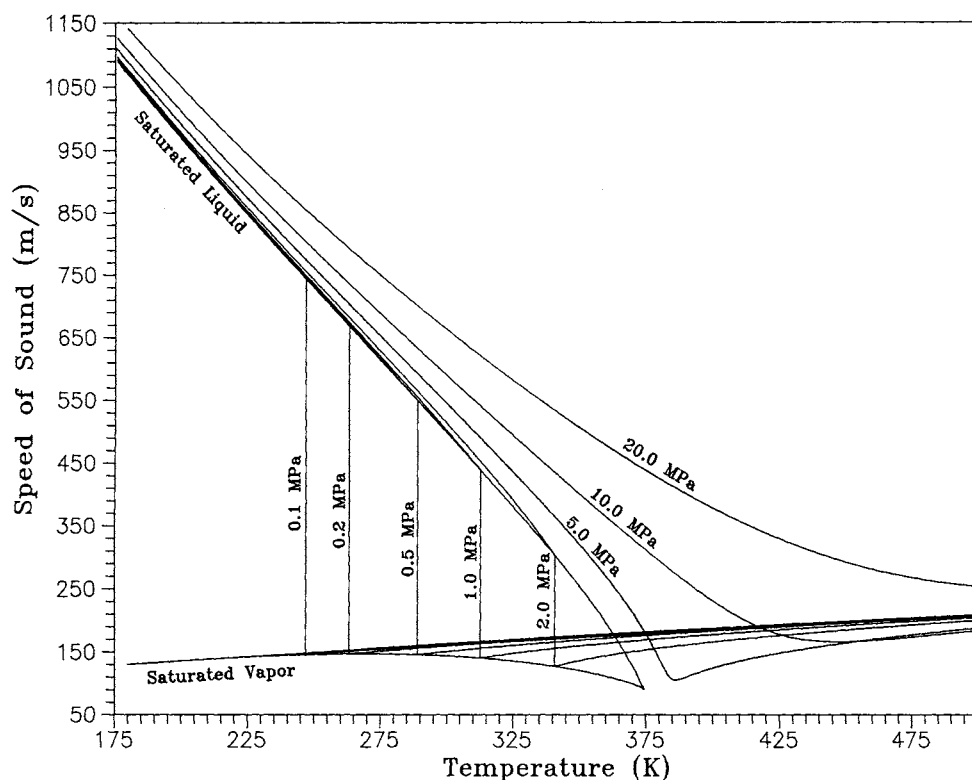


Figure 18.7 Sound speeds for HFC-134a calculated from the equation of state of Tillner-Roth and Baehr (35).

Most modern reference equations of state yield reasonable extrapolation behavior up to the limits of chemical stability of the corresponding substance. However, in general, multiparameter equations of state should not be extrapolated beyond the given range of validity, especially when using older equations or equations without an optimized functional form. When extrapolation is necessary, the reliability of the results must be checked carefully, unless reasonable extrapolation behavior is explicitly stated by the authors of the equation.

18.9 RECOMMENDED MULTIPARAMETER EQUATIONS OF STATE

Table 18.2 lists sources of recommended multiparameter equations of state which are suitable for use in system design and analysis and in scientific applications.

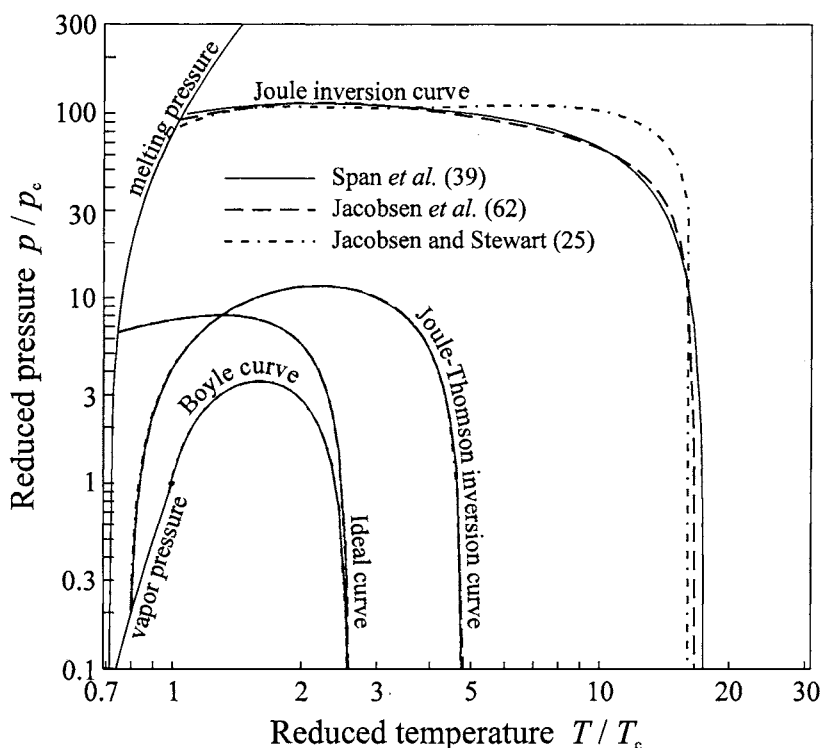


Figure 18.8 Ideal curves calculated from three different generations of reference equations for nitrogen.

In the opinions of the authors, these are the most accurate published equations available for the corresponding substances. However, depending on the available experimental data and the correlation techniques used, the accuracy of the individual equations could vary significantly. To assess whether an equation is suitable for a certain application or not, details given in the original publications should be considered.

18.10 EQUATIONS OF STATE FOR MIXTURES

There are many practical systems of mixtures of two or more fluids. Thermodynamic properties of a mixture of fluids may be defined as functions of temperature, pressure, and composition. A mixture equation of state should provide an accurate representation of the thermodynamic properties of the mixture over a wide range of compositions, including liquid and vapor properties.

Although the major emphasis of this chapter is pure fluid properties, some examples of mixture equations of state are given below. The examples selected for presentation here are illustrative of practical equations, and are not exhaustive. They provide a framework for future

Table 18.2 Wide-range thermodynamic property formulations for scientific and engineering applications.

Fluid	Author	Temperature Range (K)	Maximum Pressure (MPa)	Temperature Scale
Air	Lemmon <i>et al.</i> (63)	60 - 2000	2000	1990
Ammonia	Baehr and Tillner-Roth (30)	195 - 700	1000	1990
Argon	Tegeler <i>et al.</i> (46)	83 - 700	1000	1990
Carbon Dioxide	Span and Wagner (45)	216 - 1100	800	1990
Fluorine	de Reuck (64)	53 - 300	20	1968
Helium	McCarty and Arp (65,66)	2.18 - 1500	100	1976
Hydrogen	McCarty (67)	14 - 500	40	1968
Hydrogen Sulfide	Starling (68)	188 - 588	55	1968
Neon	Katti (69)	24 - 700	700	1968
Nitrogen	Span <i>et al.</i> (39)	63 - 1000	2200	1990
Nitrogen	Younglove (70)	66 - 500	50	1968
Trifluoride				
Oxygen	Schmidt and Wagner (33)	54 - 300	82	1968
Parahydrogen	Younglove (70)	14 - 400	121	1968
Water	Wagner and Pruss (31, 32)	273 - 1273	1000	1990
Methane	Setzmann and Wagner (44)	90 - 625	1000	1990
Ethane	Friend <i>et al.</i> (71)	90 - 623	69	1968
Propane	Younglove and Ely (72)	85 - 600	100	1968
n-Butane	Younglove and Ely (72)	134 - 500	70	1968
i-Butane	Younglove and Ely (72)	113 - 600	35	1968
n-Pentane	Span and Wagner (73)	143 - 573	69	1990
i-Pentane	Starling (68)	199 - 588	55	1968
n-Hexane	Span and Wagner (73)	177 - 548	92	1990
n-Heptane	Span and Wagner (73)	182 - 523	100	1990
n-Octane	Span and Wagner (73)	216 - 548	96	1990
Ethylene	Smukala <i>et al.</i> (47)	104 - 450	300	1990
Propylene	Angus <i>et al.</i> (74)	100 - 600	200	1968
Cyclohexane	Penoncello <i>et al.</i> (75)	279 - 700	80	1968
CFC-11	Jacobsen <i>et al.</i> (76)	162 - 625	30	1990
CFC-12	Penoncello <i>et al.</i> (77)	173 - 600	70	1990
HCFC-22	Kamei <i>et al.</i> (78)	120 - 550	60	1990
HFC-23	Penoncello <i>et al.</i> (79)	118 - 475	120	1990
CFC-113	Marx <i>et al.</i> (80)	237 - 525	200	1990
HFC-32	Tillner-Roth and Yokozeki (81)	136 - 435	70	1990
HCFC-123	Younglove and McLinden (82)	166 - 500	40	1990
HCFC-124	de Vries <i>et al.</i> (83)	100 - 400	40	1990
HFC-125	Sunaga <i>et al.</i> (84)	172 - 500	60	1990
HFC-134a	Tillner-Roth and Baehr (35)	169 - 500	70	1990
HFC-143a	Lemmon and Jacobsen (14)	161 - 500	60	1990
HFC-152a	Tillner-Roth (85)	154 - 435	30	1990

development of mixture formulations based on accurate wide range pure fluid equations of state as engineering requirements are identified. Other chapters in this book deal with mixing rules and similar details of other mixture property formulations.

18.10.1 The Virial Equation of State for Mixtures

Unlike other empirical equations of state, the virial equation of state may be developed from kinetic theory. This equation expresses the deviations from the perfect gas equation as an infinite power series in density or volume

$$\frac{P}{\rho RT} = 1 + B_m \rho + C_m \rho^2 + D_m \rho^3 + \dots \quad (18.67)$$

where the virial coefficients, B_m , C_m , D_m , ..., are functions of temperature and the subscript m refers to the mixture. B_m is the mixture second virial coefficient, C_m the third, D_m the fourth, and so on. The second and third virial coefficients are usually sufficient to represent vapor properties up to densities of about half the critical density. Coefficients beyond the third virial coefficient are not generally available from experiment. Thus, this equation of state is not practical for wide range formulations. Ideal gas behavior is represented by the virial equation as the density approaches zero.

The second and third mixture virial coefficients are defined by mixing rules from statistical mechanics as

$$B_m = \sum_i \sum_j x_i x_j B_{ij} \quad (18.68)$$

$$C_m = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk} \quad (18.69)$$

For a binary mixture, the second and third mixture virial coefficients are

$$B = x_1^2 B_{11} + x_1 x_2 (B_{12} + B_{21}) + x_2^2 B_{22} \quad \text{and} \quad (18.70)$$

$$C = x_1^3 C_{111} + x_1^2 x_2 (C_{112} + C_{121} + C_{211}) + x_1 x_2^2 (C_{122} + C_{212} + C_{221}) + x_2^3 C_{222} \quad (18.71)$$

where B_{11} , B_{22} , C_{111} , and C_{222} are the second and third virial coefficients of the pure components 1 and 2. Since the coefficients represent the effects of molecular interactions, the 1-2 and 2-1 interactions are identical: $B_{12} = B_{21}$, $C_{112} = C_{121} = C_{211}$, and $C_{122} = C_{212} = C_{221}$. The cross terms B_{12} , C_{112} , and C_{122} are related to interactions between unlike molecules and cannot be determined from the properties of the pure substances. These cross terms are usually determined from experimental mixture data.

18.10.2 Extended Corresponding-States Methods

Ely (86) and Clarke *et al.* (87) expanded on the extended corresponding states work of Leach (88) to predict the thermodynamic properties of a mixture by assuming that the mixture

behaves as a hypothetical equivalent pure substance. To determine mixture properties, the states or properties of the mixture, identified by the subscript m, and those of a reference fluid, designated by subscript o, must be in correspondence:

$$\alpha_m^r(\delta_m, \tau_m) = \alpha_o^r(\delta_o, \tau_o) = \alpha_o^r(\delta_m \phi_m, \tau_m \theta_m) \quad (18.72)$$

$$Z_m(\delta_m, \tau_m) = Z_o(\delta_o, \tau_o) = Z_o(\delta_m \phi_m, \tau_m \theta_m) \quad (18.73)$$

Corresponding states are found using shape factors, ϕ_m and θ_m , which relate the reduced properties of the mixture to those of the reference fluid. The thermodynamic properties for the mixture are reduced by the pseudo-critical parameters ρ_{cm} and T_{cm} defined as

$$\rho_{cm} = \left[\sum_p \sum_q \left(\frac{x_p x_q}{\rho_{cpq}} \right) \right]^{-1} \quad (18.74)$$

$$T_{cm} = \frac{\sum_p \sum_q x_p x_q T_{cpq} / \rho_{cpq}}{\sum_p \sum_q x_p x_q / \rho_{cpq}} \quad (18.75)$$

where the terms ρ_{cpq} and T_{cpq} are reduced temperatures and densities given by Clarke *et al.* (87). Exact shape factors are determined by simultaneous solution of the equations for the Helmholtz energy and compressibility factor, Equations (18.72) and (18.73), with nitrogen as the reference fluid.

18.10.3 Mixture Properties Using Helmholtz-Energy Equations of State

Lemmon and Jacobsen (89,90) developed a generalized mixture model using the equations of state for the pure fluids in the mixture and an excess function to account for the interaction between different species. The independent work of Tillner-Roth (91) describes a similar model for refrigerant mixtures. The formulation of Lemmon and Jacobsen is used here as an example because it has been applied to the calculation of mixtures for a large number of fluids, including hydrocarbons, cryogenics, and refrigerants.

The Helmholtz energy for mixtures of fluids can be calculated using

$$a = a^{\text{idmix}} + a^E \quad (18.76)$$

where the Helmholtz energy for an ideal mixture defined at constant reduced temperature and density (similar to simple corresponding states) is

$$a^{\text{idmix}} = \sum_{i=1}^n x_i \left[a_i^0(\rho, T) + a_i^r(\delta, \tau) + RT \ln x_i \right] \quad (18.77)$$

In these equations, n is the number of components in the mixture, a_i^0 is the ideal gas Helmholtz energy for component i , and a_i^r is the pure-fluid residual Helmholtz energy of component i evaluated at a reduced density and temperature defined below.

The excess contribution to the Helmholtz energy from mixing is

$$\frac{a^E}{RT} = \alpha^E(\delta, \tau, \mathbf{x}) = \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j F_{ij} \sum_{k=1}^{10} N_k \delta^{d_k} \tau^{t_k} \quad (18.78)$$

where the coefficients and exponents were obtained from nonlinear regression of experimental mixture data. The parameter F_{ij} is used in the generalization to relate the excess properties of one binary mixture to those of another. This parameter was arbitrarily set to one for mixtures of methane and ethane. With this parameter, the same set of mixture coefficients is used for all mixtures in the model. The value of the generalized factor, F_{ij} , is determined using a nonlinear fitting procedure that minimizes the sum of squares of the deviations between the equation and the data for a small selected set of experimental data.

All single phase thermodynamic properties can be calculated from the Helmholtz energy as described in Section 18.7 using the relations

$$\alpha^0 = \sum_{i=1}^n x_i \left[\frac{a_i^0(\rho, T)}{RT} + \ln x_i \right] \quad (18.79)$$

$$\alpha^r = \sum_{i=1}^n x_i \alpha_i^r(\delta, \tau) + \alpha^E(\delta, \tau, \mathbf{x}) \quad (18.80)$$

where the derivatives are taken at constant composition. Calculations of two-phase properties are described by Lemmon and Jacobsen (90). The reduced values of density and temperature for the mixture are

$$\delta = \rho / \rho_{\text{red}} \quad \text{and} \quad (18.81)$$

$$\tau = T_{\text{red}} / T \quad (18.82)$$

where ρ and T are the mixture density and temperature, respectively, and ρ_{red} and T_{red} are the reducing values,

$$\rho_{\text{red}} = \left[\sum_{i=1}^n \frac{x_i}{\rho_{c_i}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \xi_{ij} \right]^{-1} \quad (18.83)$$

$$T_{\text{red}} = \sum_{i=1}^n x_i T_{c_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \zeta_{ij} \quad (18.84)$$

The parameters ζ_{ij} and ξ_{ij} are used to define the shape of the reducing temperature line and reducing density line. These reducing parameters are not the same as the critical parameters of

the mixture and are determined simultaneously in the nonlinear fit of experimental data with the other parameters of the mixture model. The generalized model has been applied to mixtures of cryogenics and hydrocarbons, including methane through pentane, nitrogen, oxygen, argon, carbon dioxide, hydrogen, helium, hydrogen sulfide, and carbon monoxide, and to mixtures of refrigerants, including R-32, R-125, R-134a, R-143a, R-152a, as well as many of the less commonly used refrigerants. The accuracy in the model is comparable with that obtained in the pure fluid equations of state, and calculations of phase boundaries, including the composition of the equilibrium phase, is possible.

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