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Application of a Hard Sphere Equation of State to Refrigerants and Refrigerant Mixtures

Morrison and McLinden

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ABSTRACT

This note describes the application of the Carnahan-Starling-DeSantis equation of state to halogenated hydrocarbon refrigerants and their mixtures. A complete and consistent set of thermodynamic functions is derived from the p-V-T equation of state and the perfect (ideal) gas heat capacities. A thorough discussion of reference states is included for both pure materials and their mixtures. Although this model exhibits a critical point, it does not quantitatively represent properties in the critical region. Despite this limitation, this model can represent both liquid and gaseous mixtures away from their own critical points, even at conditions near to and above the critical points of their components.

Algorithms and FORTRAN routines for the use of this model are presented along with the numerical coefficients for 11 pure refrigerants and 7 mixtures. Routines for evaluating the coefficients from saturation data are included. Several examples of the application of this equation of state are presented to demonstrate its versatility. It is shown to predict the properties of pure materials well and to describe the detailed features of mixtures, both phase diagrams and thermodynamic properties. The average deviation from the tabulated saturation properties of the 11 pure refrigerants is 0.54 % for pressures, 0.09 % for liquid volumes, and 0.50 % for vapor volumes.

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NOMENCLATURE

$a(a_{ij})$	equation of state attraction parameter (between species i and j)
a_0, a_1, a_2	coefficients for the temperature dependence of a (defined by Eqn. 6.14)
A	molar Helmholtz free energy
$b(b_{ij})$	equation of state volume parameter (between species i and j)
b_0, b_1, b_2	coefficients for the temperature dependence of b (defined by Eqn. 6.15)
B, C	second and third virial coefficient
C_p, (C_p^o)	molar heat capacity at constant pressure (for the perfect gas state)
C_V	molar heat capacity at constant volume
c_0, c_1, c_2	coefficients for the temperature dependence of C_p^o (defined by Eqn. 6.16)
D, D*	determinates related to mixture critical point (defined by Eqn. 5.8a,b)
E	molar internal energy
f_{ij}	interaction parameter between species i and j
f_0, f_1	coefficients for the temperature dependence of f_{ij} (defined by Eqn. 6.17)
G	molar Gibbs free energy
G	total Gibbs free energy
H	molar enthalpy
H^e	molar excess enthalpy of mixing
I	ionization potential
ℓ	liquid phase
n	number of components in a mixture
n_i	number of moles of component i
N	total number of data values

p	pressure
p^*	arbitrary reference pressure
p^o	pressure of perfect gas state at specified temperature and volume
p_{low}, p_{up}	lower and upper bound on pressure for a physically meaningful solution of equation of state
R	gas constant
S	molar entropy
T	temperature
V	molar volume
$\mathbf{V}$	total volume
$x(x_i)$	molar composition (of species i)
y	$b/4V$
Z	compressibility factor
z_a, z_b	functions of chemical potential (defined by Eqns. 6.24 and 6.25)
Z^0, Z^1	functions in accentric factor method
α_p	coefficient of thermal expansion
β	$b/4$
β_t	isothermal compressibility
Γ	function defined by Eqn. 6.1
δ, Δ	change in a quantity
$\theta^{(i)}$	ith guess for iteration variable
$\theta^{(pos)}$, $\theta^{(neg)}$	guesses for θ giving positive and negative values of function ψ
λ_1, λ_2	constants in Eqns. 5.4 and 5.5
μ_{ij}	chemical potential of component i in phase j
σ	molecular diameter
ψ	iteration function
ω	accentric factor

ω_ℓ, ω_p, ω_v, ω_x	weighting factors for liquid volume, saturation pressure, vapor volume, and vapor composition data respectively

Subscripts

c	value at critical point, calculated value
e	experimental value
i,j	components i and j
ℓ, liq	liquid phase
m	mixture
sat	saturation conditions
v, vap	vapor phase

Superscripts

$-$	(overbar), partial molar quantity
^{o}	perfect gas state
$'$	temperature derivative
$''$	second derivative with respect to temperature
(i)	iteration index

1. INTRODUCTION

This Technical Note describes the application of an equation of state based on the hard-sphere fluid to an important class of industrial fluids, the halogenated hydrocarbon refrigerants and their mixtures. These compounds, including several azeotropic mixtures, have been developed over the past several decades and are now the dominant working fluids in refrigeration and heat pumping equipment. Recently, considerable interest has arisen in the use of non-azeotropic mixtures as working fluids because of potential efficiency improvements and operational advantages. The lack of precise information on the thermophysical behavior of these mixtures has hindered their commercial application. There is a need for a general property formulation that would be applicable to the analysis of a variety of pure refrigerants and their mixtures.

The purpose of this Note is to show how an equation of state founded on a realistic physical model can be used to describe the thermodynamic properties of a pure fluid or mixture with a minimum amount of experimental information. Such an equation can be viewed on two levels. First, it represents a correlation of experimental data. But more than merely correlating isolated data, an equation of state models the thermophysical behavior of a fluid. Such a model has built into it the virtues of thermodynamic consistency, realistic limiting behavior, and the power to predict unmeasured properties reasonably when there is limited experimental information. Unlike simple correlating schemes, an equation of state founded on a realistic physical model becomes an increasingly powerful tool as ones knowledge about a material increases. The authors

wish to emphasize, however, that there is no substitute for data; any predictive scheme, even one founded on a good physical model, can be considered only a temporary substitute for experimental information.

This Note develops a particular equation of state--a modification of the Carnahan-Starling hard sphere fluid that was first proposed by DeSantis, et al. (1976)--and applies it to the representation of refrigerant thermodynamic properties. We will refer to this as the Carnahan-Starling-DeSantis (CSD) equation of state. Much of this development is general, and can be applied to other similar equations of state. While only refrigerants are discussed here, the CSD equation of state has been applied to other classes of fluids, such as hydrocarbons and simple inorganic molecules (DeSantis, et al. 1976).

Section 2 of this Note briefly describes and compares classes of equations of state. The motivation for choosing the hard sphere reference fluid is explained. Section 3 presents mixing rules for the extension of the equation of state to mixtures and introduces an empirical interaction parameter used to account for deviations from the Lorentz mixing rules. Methods of predicting the interaction parameter from molecular data are reviewed and the need for experimental p-V-T-x data for its evaluation is emphasized. A complete set of thermodynamic functions is developed in Section 4. These formulations use only the p-V-T information of the equation of state and the heat capacity of a perfect (ideal) gas. A discussion of reference states is also included. Section 5 considers the behavior of the CSD and other equations of state near the critical point. In Section 6, the numerical implementation of the equation of state is discussed, including the determination of the pure component

parameters and the mixture interaction coefficient. A set of computer subroutines for carrying out these calculations is presented. Section 7 examines the ability of the equation of state to represent the thermodynamic characteristics of halogenated hydrocarbon refrigerants and their mixtures. Concluding remarks are presented in Section 8. Finally, the Appendices contain a tabulation of coefficients for use with the hard sphere equation of state and a listing of the FORTRAN subroutines developed for its implementation.

2. A COMPARISON OF EQUATIONS OF STATE

An equation of state represents the pressure-volume-temperature behavior of a pure material or the p-V-T-x behavior of a mixture. When combined with heat capacity information the complete thermodynamic behavior of a material (including enthalpy, entropy, Gibbs free energy, etc.) is defined. For the correlation of experimental data, an equation of state can represent all the thermodynamic properties with strict consistency, an advantage not necessarily retained when separate functions are used to correlate individual properties. An equation of state also permits reasonable evaluation of properties for which there are no measurements.

There are a number of classes of equations of state which are based on varying combinations of theory and empiricism and with varying ranges of applicability. The simplest of all equations of state is the perfect gas law:

$$\frac{pV}{RT} = 1 \tag{2.1}$$

It describes the behavior of an assembly of point masses with no intermolecular attraction or repulsion. It represents the properties of a gas in the limit of zero pressure. Depending upon ones requirements, it is useful at pressures less than 0.1 MPa; at temperatures well above the critical temperature it can be useful at higher pressures.

The elegant form of the perfect gas law is retained in the virial equation of state:

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots \tag{2.2}$$

where B and C are referred to as the second and third virial coefficients, respectively. This equation was proposed in 1885 by Thiesen to describe the behavior of gases and was shown by Kammerlingh-Onnes (1901) to represent the p-V-T properties of many gases well. Although originally empirical in origin, Mayer (1937) showed that this expression arose naturally from a statistical mechanical model. He was able to relate the experimental values of the virial coefficients to the molecular properties of the material. Typically, the virial equation is truncated at the second virial coefficient; such an expression is applicable at subcritical temperatures for pressures below about 1 MPa and for increasing pressures at higher temperatures, but only for gases. A major advantage of the virial equation of state is that second virial coefficients are known for a huge collection of materials (Dymond and Smith, 1969) and can be estimated in the absence of measured values (Hirschfelder, et al., 1954).

The reduced equations of state are a second approach. An example is the Pitzer (1957) accentric factor method:

$$\frac{pV}{RT} = Z^0(T_r, V_r) + \omega\, Z^1(T_r, V_r) \tag{2.3}$$

The functions Z^0 and Z^1 are universal functions of the reduced temperature and volume derived by correlating the measured properties of many materials; the accentric factor, ω, is an empirical device to compensate for the non-

spherical nature of the molecule. Conformal solution theory (Henderson and Leonard, 1971) and the TRAPP program recently developed at NBS (Ely and Hanley, 1981) also fall into this category. A similar idea is the scaled equation of state around the critical point (Stanley, 1971). These schemes are based on the idea that by taking molecular size, shape, and attractions into account, all materials can be compared in the same way. These forms, although rooted in a theoretical model, depend on data for real materials to define the functional relationships. Once these relationships have been defined by a set of well-characterized reference fluids, only a minimal set of properties are needed to estimate the scaled properties of other fluids. Such equations of state are appropriate at all conditions, limited only by the knowledge of the reference fluids and the ability of the scheme to compensate for the various characteristics of real fluids.

One of the largest classes of equations of state, comprising a large fraction of the industrially used expressions, are the modified van der Waals equations. The original equation was proposed in 1873 by van der Waals:

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \tag{2.4}$$

The first term compensates for the excluded volume in a bimolecular collision; in the classical interpretation, b is four times the molecular volume. The second term accounts for the attraction between molecules. Other equations in this class, such as the Relich-Kwong-Soave (1972) equation, and the Peng-Robinson (1976) equation include modifications of the second term, and use it to compensate for deficiencies in the first term in addition to accounting for

intermolecular attraction. These equations are cubic in volume, which is the lowest order of equation able to represent both liquid and vapor behavior with the same function. Although this class of equations of state has a liquid branch, the molecular volume has been derived for a gas-like fluid and thus there is no reason to expect that these equations will accurately produce the dense fluid (e.g., liquid) conditions. Indeed, Henderson (1979) has shown that such expressions are fundamentally flawed at high densities because the packing problem has not been properly addressed. Using an expression involving a large number of arbitrary parameters can improve the fit in the dense fluid region but has two disadvantages: first, it gives rise to calculation complexities and second, the physical meaning of the parameters is lost.

The final approach consists of equations of state based on a theoretical fluid which is used as a reference to which real fluid behavior is compared. In a sense this approach is the theoretical analog to the empirical reduced equation of state. The most important feature of a model fluid is not that it describe a particular real fluid exactly but that it contain the proper treatment of the high density states. The Leonnard-Jones fluid (Verlet and Levesque, 1967) is an example; it is composed of molecules that repel one another at short distances and attract one another at moderate and large distances. A second class of reference fluids are those characterized by a hard-body repulsion. The state of development of this class of equations is demonstrated by the fact that the most recent international steam tables (Haar, et al., 1984) are based on a hard convex-body equation of state.

A simple, well-characterized hard-body reference fluid, and the one on which the equation of state described in this report is based, is the hard-sphere fluid. Such a fluid exhibits an infinite repulsion force for a bimolecular collision at some distance of closest approach; there is zero net intermolecular force at greater distances. There have been extensive computer simulations of this fluid (Barker and Henderson, 1971) and statistical mechanical treatments to describe it (Reiss, 1965). There are three analytical functions associated with the hard sphere fluid: the Percus-Yevisk pressure equation (Lebowitz, 1964), the Percus-Yevick compressibility equation (Verlet, 1964), and the Carnahan-Starling (1969) pressure equation. The Carnahan-Starling form shall be used in this discussion primarily because of its familiarity to the engineering community:

$$\frac{pV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \tag{2.5}$$

where $y = b/4V$.

Although the Carnahan-Starling equation more closely represents the properties of the hard sphere fluid at highly compressed, nearly close-packed states, all the hard sphere fluid representations are equally good at lower, more physically realistic densities.

This equation was derived as a closed form solution to an infinite geometric series which was in turn based upon the virial expansion of Ree and Hoover (1964). Carnahan and Starling demonstrated that eq. (2.5) accurately describes rigid sphere behavior. In this equation, 'b' is a molecular volume.

Although it has a similar interpretation to the b in the van der Waals or Redlick-Kwong-Soave equations, it will not have the same numerical value. In the limit of large volumes this expression leads to a van der Waals-like term. The converse, however, is not true; at small volumes the van der Waals equation does not lead to eq. (2.5).

The hard-sphere equation is modified to compensate for long-range attractive forces by the addition of a second, semi-empirical term to arrive at the equation of state treated in this work:

$$\frac{pV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V + b)} \tag{2.6}$$

This form, first suggested by DeSantis, et al. (1976), was proposed for the prediction of multi-component, vapor-liquid equilibria and exhibited good agreement for simple inorganic molecules, hydrocarbons, and their mixtures. (The procedures for extending this equation to mixtures are discussed in the next section.)

The physical significance of the parameters defined by the Carnahan-Starling-DeSantis equation of state and their temperature dependence can be understood by comparing the differences between the reference and real fluids. The real fluid is not composed of molecules with a hard-sphere repulsive core. The determined value of the 'b' parameter is an effective core that is a measure of the average closest approach of molecules. In the real fluid, as the

temperature is raised, the average kinetic energy also increases and the average distance of closest approach becomes smaller; thus, the molecular size parameter will decrease with increasing temperature because of the softness of the short-range repulsion in the intermolecular potential. The parameter 'a' has the dimensions of energy per mole times volume per mole; in a spherical, non-polar molecule it would be connected to the dispersion forces. The attractive part of the real intermolecular potential can be highly directional because of dipole moments and higher-order internal charge distributions. As the temperature is raised, the strong coupling of these directional forces is 'washed out' and the average attractive force drops. The temperature dependence of 'a' is a reflection of the non-spherical character of the force between molecules. In this work the temperature dependence of 'a' and 'b' are represented by the following forms:

$$a = a_0 \exp(a_1 T + a_2 T^2) \tag{2.7}$$

$$b = b_0 + b_1 T + b_2 T^2 \tag{2.8}$$

These forms are those suggested by DeSantis, et al. (1976) with the addition of the T^2 terms. The methods of determining 'a' and 'b' as functions of temperature from experimental p-V-T data are discussed in Section 6.

This hard-sphere equation of state was selected for the present study of refrigerant properties because it has the advantages of being a simple expression based on a good physical model. With a few exceptions, the species used as refrigerants are small, nearly spherical molecules. These attributes in

turn allow only two physically significant parameters to represent both the liquid and vapor phases. The equation defines a fundamental thermodynamic relationship which, combined with perfect gas heat capacity information, allows a complete set of consistent thermodynamic properties to be evaluated. The equation of state can also be extended to mixtures.

3. THE EQUATION OF STATE AND MIXTURES

In the previous section, we have discussed the shortcomings of equations of state with the van der Waals excluded volume term and how the equation of state for the hard sphere fluid rectifies this serious physical flaw of the van der Waals model. In this section, we shall discuss how the equation of state for mixtures is produced.

The first approximation made in the application of the CSD equation of state to mixtures is the assumption that no substantive change needs to be made to represent the properties of a mixture. That is to say that there exists an effective 'a' and 'b' such that an equation of form identical to the one used for pure materials can be used for the mixture. This section will focus primarily on the evaluation of such an effective 'a' and 'b'. A different approach, accounting for the behavior of a mixture of hard spheres of differing diameters, will be mentioned briefly at the close of this section.

In the simplest mixture models, the effective molecular parameters are defined as follows:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij} \tag{3.1}$$

and

$$b = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j b_{ij} \tag{3.2}$$

When $i = j$, the values of a_{ii} and b_{ii} are those of the pure materials. The values of a_{ij} and b_{ij} can be obtained if nearly any experimental property of the mixture is known; examples will be given later in this discussion. The motivation of a mixing rule scheme is to determine the values of a_{ij} and b_{ij} without the assistance of measurements. The techniques used for predicting the mixture parameters fall into at least two classes, those rooted in a rigorous or at least a semi-rigorous physical model and those rooted in the correlation of large sets of mixture data (Fredinslund et al. 1977); the latter schemes are typically not applied to species with one carbon.

The origin of the size parameter, b_{12}, is the more obvious of the two. The closest distance of approach for two hard spheres is the sum of the two hard sphere radii which is evaluated as follows:

$$b_{12} = \frac{(b_1^{1/3} + b_2^{1/3})^3}{8} \tag{3.3}$$

In this Note, Eqn. 3.3 is approximated as:

$$b_{12} = (b_1 + b_2)/2 \tag{3.4}$$

This approximation has been made primarily for mathematical simplicity. When the values for 'b' are similar for the two components, the two mixing rule schemes can barely be distinguished. Unless the molecular volumes differ by more than 42 %, Eqn. 3.3 and Eqn. 3.4 will not differ by more than 1 %; and, hence, will not give rise to more than a 1/2 % difference in the value of b.

The physical origin of the mixing scheme for a_{12} has its origin in a variety of molecular and quantum mechanical models. In the equation of state, the value of 'a' arises from the attraction between the molecules. On a molecular level, the interaction energy is typically expressed as a correction to the geometric mean of the pure component energy force constants:

$$a_{12} = (1 - f_{12})(a_{11}a_{22})^{1/2} \tag{3.5}$$

The correction factor, $(1 - f_{12})$, attempts to account for differences in polarizability of the two species (the ease with which the two electron clouds are deformed) and the closest distance of approach. Schemes for predicting f_{12} are reviewed by Pesuit (1978), who considers them on several levels of empiricism. What is impressive is the degree to which the interaction parameter can be estimated for relatively complex molecules. Equally impressive however is the unexpected collapse of these estimation rules. Knobler (1978) has shown that even for so simple mixtures as He/Ne, He/Ar, He/Kr and He/Xe that an estimation of the interaction parameter such as the following is far from adequate:

$$(1 - f_{12}) = \frac{2(I_1 I_2)^{1/2}}{I_1 + I_2} \frac{2^6 \sigma_{11}{}^3 \sigma_{22}{}^3}{(\sigma_{11} + \sigma_{22})^6} \tag{3.6}$$

I_i is the ionization potential of component i; and σ_{ii}, the molecular diameter. The experimental value for $(1 - f_{12})$ is 0.611 for He/Xe; its predicted value is 0.824. The conclusion that one would draw from the examples given by Knobler and Pesuit are that the methods for estimating f_{12} are not

very satisfactory and that a method appropriate for one class of mixtures may not be satisfactory for another.

The thesis of these models is that all the information needed to describe the interaction between unlike species can be derived from information about the interaction between like molecules. This thesis neglects the possibility that there can be interactions in mixtures that are either unimportant or do not occur in the pure fluids; the converse is equally possible. Recently, Gubbins and his colleagues have attempted to evaluate functions related to f_{12} from the multipole-multipole interactions between molecules (Gubbins and Twu, 1978). Wallis et al. (1984) have shown that this approach can be used effectively in describing mixtures of carbon dioxide and ethane. In general, one should approach these estimation schemes with caution and in the spirit that they can be used as guides when no other information exists. One should be aware that, at present, the only quantitative estimation of a function such as f_{12} can arise from experimental information.

In this Note, the interaction parameter will be evaluated solely from experimental mixture information. Almost any small set of data on the mixture is sufficient to evaluate f_{12}. Because there is but a single parameter to evaluate for the mixture, one needs in principle only a single measurement; however, the larger the experimental data set, the greater the certitude in the evaluation of f_{12}. In section 6 of this Note, a description of the use of bubble point information to evaluate f_{12} is given. One often finds cross second virial coefficients, B_{12}, in the literature; such information can be used to find f_{12} through the appropriate expansion of the equation of state.

One can also use gas phase data. Of the available data, liquid phase densities are perhaps the least reliable because a tiny difference between the actual density and the equation of state density at the same pressure can lead to large errors in the pressure.

The above discussion has dealt with finding an effective 'a' and 'b' for a mixture for use with an expression developed for pure fluids. There are equations of state that approximate the composition dependence for mixtures of hard spheres (Mansoori and Leland, 1970) such as the following:

$$\frac{pV}{RT} = \frac{1 + (1 - 3A)y + (1 - 3B)y^2 - (1 - C)y^3}{(1 - y)^3} \tag{3.7}$$

In this equation, the various terms in the Carnahan-Starling equation have become functions of the averages of various powers of the hard sphere diameters. When the two molecular volumes differ by a factor of 1.5, A is no larger than 0.018, B no larger than .0089, and C no larger than 0.013. In the limit of a pure material, A, B, and C, become zero and Eqn. 3.7 reduces to the original Carnahan-Starling expression. In this work, we shall assume that the departure from the Carnahan-Starling equation of state caused by the disparity between the molecular sizes is unimportant and that this disparity can be compensated for in the interaction parameter f_{12}.

4. THERMODYNAMIC FUNCTIONS AND REFERENCE STATES

There are two themes found in each of the two parts of this section. The first is a general description of some important thermodynamic derivatives. In this Section on pure fluids, the derivation of the thermodynamic properties from a p-V-T equation of state is discussed. In the part on mixtures, the ideal mixture model is developed. The second theme confronts the problem of reference materials and conditions (or reference states). In the section on pure materials, the perfect gas appears as a necessary part of the derivation and, through it, other reference states are constructed. In the section on mixtures, the reference states of the components of the mixture are connected to the thermodynamic properties of the mixture.

Pure Fluids

In the previous sections, we have discussed the physical origin of the hard sphere equation of state and the merits of using such a model at high fluid densities instead of a model where the excluded volume is expressed by the van der Waals, 1/(V-b), term. We begin here a review of the derivation of the thermodynamic properties of a fluid from its p-V-T equation of state and show the specific results for the Carnahan-Starling-DeSantis equation. In this discussion we will find that the pressure equation of state does not include all the information necessary to evaluate the thermodynamic properties completely. We shall resort to the properties of the perfect gas, spectroscopic information, and relationships provided by statistical thermodynamics to form a complete set of thermodynamic functions.

The pressure is connected to the Helmholtz free energy and, through it, to all the other thermodynamic properties by the following relation:

$$p = -\left(\frac{\partial A}{\partial V}\right)_T \tag{4.1}$$

The Helmholtz free energy can be evaluated from the pressure by an integration over volume. Several difficulties are encountered in this integration: first the choice of appropriate limits for the integration, second, the possibility of divergences in the integral, and, finally, the recognition that there will be integration constants. The problems of integration limits and divergences are closely connected; they will be discussed together.

When the Helmholtz free energy is calculated, we would like to choose the limits of the integration so that one of them is independent of the form of the equation of state. This can be achieved by having one limit be $V = \infty$, where all gases become perfect gases*. At that limit, however, the integral diverges. This problem can be resolved by evaluating the difference between the properties of the fluid described by the equation of state and those of the perfect gas. As the volume approaches infinity, this difference becomes zero sufficiently strongly that the integral remains finite. Thus,

$$p - p^o = p - \frac{RT}{V} = -\left(\frac{\partial}{\partial V}(A - A^o)\right)_T \tag{4.2}$$

---

*The term 'perfect gas' is used rather than 'ideal gas' in order to preserve the term 'ideal' for certain properties of mixtures.

and

$$A(V,T) - A^{o}(V,T) = \int_{V}^{\infty} (p - \frac{RT}{V})dV \tag{4.3}$$

Throughout this section, functions applicable to the Carnahan-Starling-DeSantis equation of state (such as those evaluated by Equations 4.2 and 4.3) are given in Table 4.1.

Before evaluating the remaining functions, let us review the features of the Helmholtz free energy calculation. First, in performing the integration, we have resorted to a reference material, the perfect gas. It was chosen to avoid a divergent integral. Although the perfect gas is a construct, it is a convenient and useful material against which to compare the properties of any other material--all gases become perfect gases in the $V = \infty$ limit and its properties are known to the last detail. The second feature of the integration is a more general consequence of that operation. Since the integral was over volume, both $A(V,T)$ and $A^{o}(V,T)$ may be in part functions that are independent of volume. Because the difference between the two free energies is uniquely defined, the temperature dependent and volume independent parts of $A(V,T)$ and $A^{o}(V,T)$ must be identical. Unless one is aware of these functions which are constants with respect to the volume integration, other thermodynamic functions will not be complete.

Once the Helmholtz free energy has been evaluated, all the other thermodynamic functions arise by the usual operations

$$S = -\left(\frac{\partial A}{\partial T}\right)_V \tag{4.4a}$$

$$S - S^o = -\left(\frac{\partial}{\partial T}\ (A - A^o)\right)_V \tag{4.4b}$$

and

$$E = A + TS \tag{4.5a}$$

$$E - E^o = (A - A^o) + T(S - S^o) \tag{4.5b}$$

and

$$H = E + pV \tag{4.6a}$$

$$H - H^o = (E - E^o) + (pV - RT) \tag{4.6b}$$

and

$$G = A + pV \tag{4.7a}$$

$$G - G^o = (A - A^o) + (pV - RT) \tag{4.7b}$$

The values of the functions in Equations 4.4b, 4.5b, 4.6b, and 4.7b are given in Table 4.1. The reference material for the functions enumerated in these equations has, in all cases, been the perfect gas at the same temperature and volume as the real fluid. For E and H, the perfect gas values depend only on temperature, hence, volume is deleted as an appropriate argument for those

properties in Table 4.1. The reference condition for the Gibbs free energy is often chosen terms of a fixed pressure. This choice arises because of the role of the Gibbs free energy in determining phase equilibrium. Equation 4.7b can be easily modified to account for a reference pressure, p*, as follows:

$$G(V,T) - G^{o}(V,T) = G(V,T) - G^{o}\left(p = \frac{RT}{V},\ T\right)$$

$$= G(V,T) - G^{o}(p,T) + G^{o}(p^{*},T) - G^{o}(p^{*},T)$$

$$= G(V,T) - G^{o}(p^{*},T) - RT\ \ell n\left(\frac{RT}{p^{*}V}\right)$$

or

$$G(V,T) - G^{o}(p^{*},T) = RT\ \ell n\left(\frac{RT}{p^{*}V}\right) + G(V,T) - G^{o}(V,T) \tag{4.8}$$

This function can be found in Table 4.1.

The heat capacity at constant volume is evaluated as follows:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{4.9a}$$

$$C_V - C_V^{o} = \left(\frac{\partial}{\partial T}(E - E^{o})\right)_V = T\left(\frac{\partial}{\partial T}(S - S^{o})\right)_V \tag{4.9b}$$

Earlier in this section, the need to recognize the existence of volume independent functions as a consequence of the calculation of the Helmholtz

free energy from the pressure was noted. It is in the evaluation of the heat capacities that the existence of these functions becomes most apparent. The perfect gas has both internal energy and a heat capacity, yet both are independent of the volume.

$$\left(\frac{\partial E^o}{\partial V}\right)_T = T\left(\frac{\partial p^o}{\partial T}\right)_V - p^o = \frac{RT}{V} - \frac{RT}{V} = 0 \tag{4.9a}$$

$$\left(\frac{\partial C_v^o}{\partial V}\right)_T = \frac{\partial^2 E^o}{\partial V \partial T} = \frac{\partial^2 E^o}{\partial T \partial V} = T\left(\frac{\partial^2 p^o}{\partial T^2}\right)_V = 0 \tag{4.9b}$$

The perfect gas values of E and C_V as well as H and C_p and parts of A, G, and S can be evaluated from calorimetric measurements, however, these quantities are typically calculated through straight-forward statistical mechanical relationships from infrared and Raman Spectra of low pressure gases.

The heat capacity at constant pressure can be calculated from the enthalpy or entropy at constant pressure

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{4.10a}$$

however, because the equation of state is a function explicit in temperature and volume, C_p is more readily evaluated from C_V and temperature and volume derivatives of the pressure:

$$C_p = C_V - T\left(\frac{\partial p}{\partial T}\right)_V^2 \Big/ \left(\frac{\partial p}{\partial V}\right)_T \tag{4.10b}$$

From the beginning of this derivation we have been forced to choose a reference material. The initial choice, the perfect gas, was made to avoid a divergence in the value of an integral. There may be reasons for choosing other reference conditions. Some properties require no reference, properties such as pressure, volume, temperature, and heat capacity can be measured absolutely. Indeed, the reason for using the perfect gas reference for heat capacity is that it can be determined quite accurately. Other properties have only relative measures; a zero value has a significance only by convention. For these properties, only changes can have any physical significance. Among these are internal energy, enthalpy, and entropy. The two free energies present a very special problem. A change of G when temperature is kept constant requires knowing the volume. A change of A at constant temperature requires the pressure, obviously there is no problem in either case. When the temperature is changed, however, the value of S must be known. Depending upon ones interpretation of the statement of the third law of thermodynamics, one can debate whether the entropy has a known absolute value or not, surely its value relative to a special state at 0 K is known. Thus changes in G and A cannot be calculated without carrying an unknown quantity T S(0 K). Fortunately, one uses G and A only in fixed temperature processes. We have then at least three kinds of thermodynamic functions: those known absolutely, those known only relative to a state at the same temperature; and those known relative to a state at a different temperature.

One may have special reasons for choosing a particular reference condition. One might choose a readily accessible physical state. For example, the reference state in chemical thermodynamics is often the element in its stable form as found at 101.33 kPa and 25°C. In electrochemistry, all voltages are typically compared to the standard hydrogen electrode. For gases, one might choose the perfect gas at 101.33 kPa and 25°C. For refrigerants the reference is typically the liquid at its saturation pressure at -40°C. There are, of course, as many reference states as there are applications for thermodynamics; they are all interconnected through thermodynamic relationships. Some of these reference states carry the weight of an internationally accepted definition and are often referred to as STANDARD STATES. The significance of a STANDARD STATE is its widespread use and precise definition.

The next few paragraphs will be devoted to examples in which the enthalpy, internal energy, and the entropy are calculated with respect to an arbitrary reference temperature, T_{ref}, and reference pressure, p_{ref}. Since the pressure is an explicit function of volume and since several states of a material may have the same pressure, the description of the reference state is further defined by indicating the volume parenthetically after the pressure.

The most effective way to go from one thermodynamic state to another is to break the path into steps for which a single variable is changed at a time and for which the changes are readily calculated. For example, for the enthalpy

$$
\begin{aligned}
H(p(V),T) = {} & H(p(V),T) - H^{o}(T) \\
& + H^{o}(T) - H^{o}(T_{ref}) \\
& + H^{o}(T_{ref}) - H(p_{ref}(V_{ref}),\ T_{ref}) \\
& + H(p_{ref}(V_{ref}),\ T_{ref})
\end{aligned}
\tag{4.11}
$$

The terms in the first and third lines on the right hand side of Equation 4.11 can be evaluated according to the enthalpy expressions in Table 4.1. The second line involves the integral of C_p^o between the two temperatures, T and T_{ref}. The final term is the reference enthalpy, which may be set to zero by convention or is more properly moved to the left hand side of the equation. We have then

$$
\begin{aligned}
& H(p(V),T) - H(p_{ref}(V_{ref}),\ T_{ref}) = \\
& \quad [H(p(V),T) - H^{o}(T)] \\
& \quad + \int_{T_{ref}}^{T} C_p^o \, dT \\
& \quad - [H(p_{ref}(V_{ref}),\ T_{ref}) - H^{o}(T_{ref})]
\end{aligned}
\tag{4.12}
$$

Internal energy can be evaluated in a similar fashion

$$
\begin{aligned}
& E(V,T) - E(V_{ref},\ T_{ref}) = \\
& \quad [E(V,T) - E^{o}(T)] \\
& \quad + \int_{T_{ref}}^{T} C_v^o \, dt \\
& \quad -[E(V_{ref},\ T_{ref}) - E^{o}(T_{ref})]
\end{aligned}
\tag{4.13}
$$

As in the case of enthalpy, the first and third lines on the right hand side of this expression are found in Table 4.1.

The derivation of the entropy is similar, however it has an additional term because, unlike H^o and E^o, S^o is not independent of volume.

$$
\begin{aligned}
S(V,T) = {} & S(V,T) - S^o(V,T) \\
& + S^o(V,T) - S^o(V_{ref},T) \\
& + S^o(V_{ref},T) - S^o(V_{ref}, T_{ref}) \\
& + S^o(V_{ref}, T_{ref}) - S(V_{ref}, T_{ref}) \\
& + S(V_{ref}, T_{ref})
\end{aligned}
\tag{4.14}
$$

In this expression, the first and fourth terms are given in Table 4.1, the third term is the integral of $C_V^o(T)/T$, and V_{ref} is the volume at the reference state (e.g., for refrigerants, the saturation volume of the liquid at T_{ref}). The second term is evaluated as follows:

$$
S^o(V,T) - S^o(V_{ref},T) = \int_{V_{ref}}^{V} \left(\frac{\partial S^o}{\partial V}\right)_T dV \tag{4.15}
$$

The Maxwell relation allows this derivative, $(\partial S/\partial V)_T$ to be evaluated in a straightforward manner.

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V \tag{4.16}$$

For the perfect gas:

$$-\left(\frac{\partial p}{\partial T}\right)_V = -\frac{R}{V}$$

The second term then becomes

$$S^o(V,T) - S^o(V_{ref},T) = -\int_{V_{ref}}^{V}\left(\frac{R}{V}\right)dV = -R\ln\left(\frac{V}{V_{ref}}\right)$$

The quantity that appears in the refrigerant property tables is as follows:

$$S(V,T) - S(V_{ref},\ T_{ref}) =$$

$$[S(V,T) - S^o(V,T)] - R\ln\left(\frac{V}{V_{ref}}\right)$$

$$+ \int_{T_{ref}}^{T}\left(\frac{C_V^o}{T}\right)dT$$

$$- [S(V_{ref},\ T_{ref}) - S^o(V_{ref},\ -T_{ref})] \tag{4.17}$$

Table 4.1 Thermodynamic Functions Arising from the Perturbed Carnahan-Starling Equation of State

$$\frac{pV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V + b)}$$

$$y = b/4V$$

$$A(V,T) - A^o(V, T) = -\frac{a}{b}\ln\left(\frac{V + b}{V}\right) + \frac{4RT\beta}{(V - \beta)} + \frac{RT\beta^2}{(V - \beta)^2}$$

$$\beta = b/4$$

$$G(T,p(V)) - G^o(p^*,T) = RT\ln\left(\frac{RT}{p^*V}\right) - \frac{a}{b}\ln\left(\frac{V + b}{V}\right) + \frac{RT\beta}{(V - \beta)^3}(8V^2 - 9V\beta + 3\beta^2) - \frac{a}{V + b}$$

$$\mu(T,p(V),x_i) = G(T,p(V),x_i) + (1 - x_i)\left(\frac{\partial G}{\partial x_i}\right)_{T,p}$$

$$= \mu^o(p^*,T,x_i) + RT\ln\left(\frac{RT}{p^*V}\right) + \frac{RT\beta(4V - 3\beta)}{(V - \beta)^2} + \frac{RT\beta_i(4V^2 - 2V\beta)}{(V - \beta)^3} + \frac{ab_i}{b^2}\ln\left(\frac{V + b}{V}\right)$$

$$- \frac{ab_i}{b(V + b)} + \frac{2x_ia_i + 2x_ja_{ij}}{b}\ln\left(\frac{V}{V + b}\right)$$

Note: the above expression for chemical potential applies only to a binary mixture.

$$S(V,T) - S^o(V,T) = \frac{a'b - ab'}{b^2}\ln\left(\frac{V + b}{V}\right) + \frac{ab'}{b(V + b)} - \frac{R\beta(4V - 3\beta)}{(V - \beta)^2} - \frac{RT\beta'(4V^2 - 2V\beta)}{(V - \beta)^3}$$

$$E(V,T) - E^o(T) = \frac{a'bT - ab'T - ab}{b^2}\ln\left(\frac{V + b}{V}\right) + \frac{ab'T}{b(V + b)} - \frac{RT^2\beta'(4V^2 - 2V\beta)}{(V - \beta)^3}$$

$$H(T,p(V)) - H^o(T) = \frac{ab'T - a'bT - ab}{b^2}\ln\left(\frac{V + b}{b}\right) + \frac{ab'T - ab}{b(V + b)} + \frac{RT(4V^2 - 2V\beta)(\beta - \beta'T)}{(V - \beta)^3}$$

$$C_V(V,T) - C_V^o(T) = \frac{6RT^2\beta'^2(V\beta - 2V^2)}{(V - \beta)^4} + \frac{2RTV((\beta''T + 2\beta')(\beta - 2V) + \beta'^2T)}{(V - \beta)^3} - \frac{Tab'}{b(V + b)^2}$$

$$+ \frac{T(ab''b + 2a'b'b + 2ab'^2)}{b^2(V + b)} - \frac{(a''b^2T - 2a'b'bT + 2ab'^2T - ab''bT)}{b^3}\ln\left(\frac{V + b}{V}\right)$$

$$C_p = C_V - T\left(\frac{\partial p}{\partial T}\right)^2_{V,x} \Big/ \left(\frac{\partial p}{\partial V}\right)_{T,x}$$

NOTE: primed quantities indicate a temperature derivative; double primed quantities are second derivatives with respect to temperature.

The Thermodynamic Properties of Mixtures

The above discussion presented in detail for a pure substance: 1) the calculation of thermodynamic properties from an equation of state, 2) the perfect gas state, 3) reference states.

In this section, the discussion will be expanded to include the thermodynamic properties of mixtures. The discussion of mixtures in many ways will parallel that for pure materials but will differ in two important ways because of the extra degree(s) of freedom accessible to mixtures, the compositions. The first topic to be discussed will be reference states for mixtures. Integral to that discussion will be the description of a special class of mixture, the ideal mixture. The second topic that will be covered is the class of thermodynamic properties, the partial molar properties, that arise from the derivatives of extensive properties with respect to changes in the composition. In this class of properties, the chemical potential will be needed to evaluate conditions of phase equilibrium.

If the components of a mixture did not tend to separate during a phase transition, one could define reference states for mixtures in the same way that such states are defined for pure materials. To use refrigerant materials as an example, one could choose the liquid phase at its bubble pressure at -40°C. The incipient vapor in equilibrium with that liquid typically has a different composition. If that vapor were condensed and its reference point were defined as the liquid at its own bubble pressure at -40°C, one would implicitly have changed the reference point of the parent liquid phase; chaos would follow! The following paragraphs discuss a solution to this dilemma.

The properties of pure materials were initially tied to the properties of the perfect gas. Through that connection, the properties of the material at any two arbitrary states are automatically connected. The properties of mixtures will be connected to the properties of their constituent components through the ideal mixture. In the discussion of the ideal mixture, we shall find that the ideal mixture of perfect gases will be particularly useful.

The properties of the ideal mixture can be described in terms of the following simple experiment: the mixing of the pure constituents all at the same temperature and pressure, to form a mixture at the same temperature and pressure. Regardless of the composition, temperature, or pressure, one would find for an ideal mixture that first, the final volume of the mixture would equal the sum of the volumes of the unmixed components. That is,

$$V_m(T,p,\{x_i\}) - \sum_i x_i V_i(T,p) = 0 \tag{4.18}$$

(Where V_i is the molar volume of component i or the mixture and x_i is the mole fraction of the respective component in the mixture.)

Secondly, the mixture would have to be neither heated nor cooled to bring it to the same temperature as the unmixed components; the enthalpy of the mixture would be the same as the sum of the enthalpies of its constituent pure components:

$$H_m(T,p,\{x_i\}) - \sum_i x_i H_i(T,p) = 0 \tag{4.19}$$

By multiplying Eqn. 4.18 by the pressure and then subtracting the result from Eqn. 4.19 we have a similar relationship for the internal energy, E.

$$E_m(T,V_m(p),\{x_i\}) - \sum_i x_i E_i(T,V_i(p)) = 0 \tag{4.20}$$

When the temperature derivatives at constant pressure are taken of Eqns. 4.18 and 4.19, one finds similar relations for the coefficients of thermal expansion (weighted by the molar volume) and the heat capacity at constant pressure.

$$V_m(T,p,\{x_i\})\ \alpha_{pm}(T,p,\{x_i\}) - \sum_i x_i V_i(T,p)\ \alpha_{pi}(T,p) = 0 \tag{4.21}$$

(Where α_p is the coefficient of thermal expansion of the respective component or mixture, $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$.)

$$C_{pm}(T,p(V),\{x_i\}) - \sum_i x_i C_{pi}(T,p(V)) = 0 \tag{4.22}$$

(Where C_p is the molar heat capacity at constant pressure of the respective component or mixture.)

When the pressure derivative at constant temperature is taken of Eqn. 4.18, a linear relation for the isothermal compressibilities (weighted by the molar volumes) can be derived:

$$V_m(T,p,\{x_i\})\beta_{Tm}(T,p,\{x_i\}) - \sum_i x_i V_i(T,p)\beta_{Ti}(T,p) = 0 \tag{4.23}$$

(Where β_T is the isothermal compressibility of the respective component or mixture, $-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$.)

A similar relationship can be derived for the molar heat capacity at constant volume. The simple linear relationship is valid, however, only under very restricted conditions. By using the following relation between C_v and C_p:

$$C_v = C_p + TV\,\alpha_p^2/\beta_T \tag{4.24}$$

the first term on the right-hand-side is linear in composition for ideal mixtures (Eqn. 4.22). The second term can be made linear with respect to the composition only if both the numerator and the denominator are insensitive to the composition. Except for a truly unusual liquid mixture, the only material that satisfies such a requirement is the perfect gas. The perfect gas thus plays a central role in connecting the properties of the mixture to those of its constituent components. For perfect gas mixtures,

$$C_{Vm}(T,V(p),\{x_i\}) - \sum_i x_i C_{Vi}(T,V_i(p)) = 0 \tag{4.25}$$

(Where C_V is the molar heat capacity at constant volume for the respective component or mixture.)

There is one further property of the ideal mixture, the entropy of mixing.

$$S_m(T,p(V),\{x_i\}) - \sum_i x_i S_i(T,p(V)) = -R\sum_i x_i \ln(x_i) \tag{4.26}$$

By comparing Eqns. 4.19 and 4.26, the Gibbs free energy associated with mixing is as follows:

$$G_m(T,p(V),\{x_i\}) = H_m(T,p(V),\{x_i\}) - TS_m(T,p(V),\{x_i\})$$

or

$$G_m(T,p(V),\{x_i\}) - \sum_i x_i G_i(T,p(V)) = RT\sum_i x_i \ln(x_i) \tag{4.27}$$

The definition of the properties of the ideal mixture allow the real mixture properties and the real pure component properties to be connected, whether it be the pure components at the same temperature and pressure or the pure components under some other conditions, in particular, their respective reference states. The details for determining the mixture equation of state have been discussed in Section 3 of this Technical Note. Once the form of the equation of state has been established, all the thermodynamic properties of the fluid mixture with reference to the respective properties of a perfect gas mixture with the same composition can be evaluated by using the formalism described earlier in this Section. Two examples follow: the evaluation of the enthalpy of the mixture first with respect to the enthalpy of the pure components at the same temperature and pressure as the mixture and then with respect to a reference state of the pure materials. For the sake of simpli-

city, a binary mixture will be discussed; this example may be expanded to any number of components.

$$
\begin{aligned}
H_m(T,p(V),x_1) = {} & H_m(T,p(V),x_1) - H_m^o(T,x_1) \\
& + H_m^o(T,x_1) - x_1 H_1^o(T) - (1 - x_1) H_2^o(T) \\
& + x_1 [H_1^o(T) - H_1(T,p(V_1))] \\
& + (1 - x_1)[H_2^o(T) - H_2(T,p(V_2))] \\
& + x_1 H_1(T,p(V_1)) + (1 - x_1) H_2(T,p(V_2)) \qquad (4.28)
\end{aligned}
$$

By inspection, one can see that this expression reduces to the identity $H_m(T,p(V),x_1) = H_m(T,p(V),x_1)$. The first, third, and fourth line of the right-hand-side of Eqn. 4.28 can be evaluated using the functions in Table 4.1 and the appropriate values for the equation of state parameters, a and b. The second line equals zero because a perfect gas mixture is ideal. The final line is the weighted sum of the enthalpies of the pure fluids at the same temperature and pressure as the mixture. The sum of the first, third and fourth lines in the right-hand-side of Eqn. 4.28 is the enthalpy of mixing of the components '1' and '2' at fixed T and p. A simple expansion of the calculation that led to Eqn. 4.28 produces the value of the enthalpy of the mixture with respect to the reference pressure and temperature of its constituent components, as follows:

$$
\begin{aligned}
H_m(T, p(V), x_1) = {} & H_m(T, p(V), x_1) - H_m^o(T, x_1) \\
& + H_m^o(T, x_1) - x_1 H_1^o(T) - (1 - x_1) H_2^o(T) \\
& + x_1 [H_1^o(T) - H_1^o(T_{1,ref}) \\
& \quad + H_1^o(T_{1,ref}, p) - H_1^o(T_{1,ref}, p_{1,ref}) \\
& \quad + H_1^o(T_{1,ref}) - H_1(T_{1,ref}, p_{1,ref}(V_{1,ref}))] \\
& + (1 - x_1) \text{ [terms for component 2 similar to those for component 1]} \\
& + x_1 H_1(T_{1,ref}, p_{1,ref}(V_{1,ref})) \\
& + (1 - x_1) H_2(T_{1,ref}, p_{2,ref}(V_{2,ref})) \qquad (4.29)
\end{aligned}
$$

In this expression, the first and second lines are identical to those in Eqn. 4.28; the third line is the integral of the perfect gas molar heat capacity at constant pressure between the temperature of interest and the reference temperature for component 1. The next line equals zero because of the properties of the perfect gas. The fifth line can be evaluated using Table 4.1. A similar set of terms exists for the second component. The final two terms on the right hand side of Eqn. 4.29 represent the pure components in their respective reference states. The enthalpy of the mixture then becomes the following:

$$H_m(T,p(V),x_1) = H_m(T,p(V),x_1) - H_m^o(T,x_1)$$

$$+ x_1[\int_{T_{1,ref}}^{T} C_{p1}^o(T)\,dT + H_1^o(T_{1,ref}) - H_1(T_{1,ref},p_{1,ref}(V_{1,ref}))]$$

$$+ (1 - x_1) \quad \text{[terms for component 2 similar to those for component 1]}$$

$$+ x_1 H_1(T_{1,ref},p_{1,ref}(V_{1,ref}))$$

$$+ (1 - x_1) H_2(T_{2,ref},p_{2,ref}(V_{2,ref})) \tag{4.30}$$

The last two terms cannot be determined absolutely. Setting such terms equal to zero is an arbitrary assignment of the reference state. More properly, these terms should be moved to the left-hand side of the equation.

The entropy for the mixture is evaluated as follows:

$$S_m(T,p(V),x_1) = S_m(T,p(V),x_1) - S_m^o(T,V,x_1)$$

$$+ S_m^o(T,V,x_1) - x_1 S_1^o(T,V) - (1 - x_2) S_2^o(T,V)$$

$$+ x_1[S_1^o(T,V) - S_1^o(T_{1,ref},V)$$

$$+ S_1^o(T_{1,ref},V) - S_1^o(T_{1,ref},V_{1,ref})$$

(continued on next page)

$$- S_1(T_{1,ref}, P_{1,ref}(V_{1,ref})) - S_1^o(T_{1,ref}, V_{1,ref})]$$

$$+ (1 - x_1) \text{ [terms for component 2 similar to those for component 1]}$$

$$+ x_1 S_1(T_{1,ref}, p_{1,ref}(V_{1,ref}))$$

$$+ (1 - x_2) S_2(T_{2,ref}, P_{2,ref}(V_{2,ref})) \tag{4.31}$$

The path that is followed in the calculation is the same as for the enthalpy. The first, and fifth lines can be evaluated from Table 4.1 by substituting the appropriate values for the molecular parameters into the equation of state. The second line can be evaluated from Eqn. 4.26. The third line is evaluated by integrating C_V^o/T over the temperature range T_{ref} to T. The fourth line is evaluated by integrating $(\partial S/\partial V)_T$ over the volume range and using the Maxwell relation that $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, which equals R/V for a perfect gas. Equation 4.31 then becomes the following:

$$S_m(T, p(V), x_1) = S_m(T, p(V), x_1) - S^o(T, V, x_1)$$

$$- R(x_1 \; n(x_1) + (1 - x_1) \ell n(1 - x_1))$$

$$+ x_1 [\int_{T_{1,ref}}^{T} \frac{C_v}{T} dT + R \; \ell n(V/V_{1,ref}))$$

$$- S_1(T_{ref}, P_{1,ref}(V_{1,ref})) - S^o(T_{ref}, V_{ref})]$$

$$+ (1 - x_1) \text{ [terms for component 2 similar to those for component 1]}$$

$$+ x_1 \; S_1 \; (T_{1,ref}, P_{1,ref}(V_{1,ref}))$$

$$+ (1 - x_1) \; S_2 \; (T_{2,ref}, P_{2,ref}(V_{2,ref})) \tag{4.32}$$

The evaluation of any mixture property proceeds by a similar method. First evaluate the difference between the real mixture and the ideal-perfect gas mixture. When the components are separated, the derived nature of the ideal mixture prescribes the associated change in the property. After the separation has been made, each component can be treated as if it were a pure material.

The additional degree(s) of freedom with mixtures, the compositions, gives rise to a set of properties that typically have a trivial meaning in pure materials, the partial molar properties. Earlier in this section, the experiment that led to the definition of the ideal mixture was discussed. Let us discuss an experiment performed under similar conditions for which the outcome is different. Suppose one had a mixture of two materials, A and B, at a particular temperature and pressure. Let us further suppose that a small amount of B were added to the mixture while keeping at T and p constant. If one measured the ensuing change in volume and attributed that change to the 'effective' volume of the added component in the mixture, that effective molar volume would be calculated as follows:

$$\bar{V}_B = [\mathbf{V}(T, p, n_A, n_B + \delta n_B) - \mathbf{V}(T, p, n_A, n_B)]/\delta n_B \tag{4.33}$$

where the bold face $\mathbf{V}$ indicates a total (rather than a molar) volume, and n_i refers to the total number of moles of the respective components. In the limit of adding an infinitesimal amount of B, the effective molar volume described in Eqn. 4.33 becomes the value of the following partial derivative:

$$\bar{V}_B = (\partial V(T,p,n_A,n_B)/\partial n_B)_{T,p,n_A} \tag{4.34}$$

This partial derivative is the definition of the 'partial molar volume'. (Partial molar quantities are indicated by an overbar.) One could have evaluated the partial molar volume of component A, $\bar{V}_A$, in terms of the partial derivative of the volume with respect to the amount of A. One can define similar partial molar quantities for any extensive property of the system. In this example, one can be comforted by the explanation that the partial molar volumes are effective volumes. Partial molar quantities often do not retain this simple interpretation; thus one should keep in mind the formal mathematical definition of these quantities.

In the previous paragraph we have discussed an operational definition for the partial molar volume. Typically, it is experimentally determined in a different way, by noting the variation of the molar volume with composition. In the following paragraphs, the connection between the molar volume and the partial molar volume will be discussed and an example of an important class of thermodynamic relationships will be encountered.

Because volume is an extensive property, more properly a first order homogeneous function of the amount, one can write the following relation between the total volume and the molar volume of a material:

$$V(T,p,n_1,n_2) = nV(T,p,\frac{n_1}{n},\frac{n_2}{n})$$

$$= nV(T,p,x_1) \tag{4.35}$$

where $n = n_1 + n_2$. The partial molar volume of the two components can be calculated as follows:

$$\bar{V}_1\ (T,p,n_1) = \left(\frac{\partial V}{\partial n_1}\right)_{T,p,n_2}$$

$$= V\ (T,p,n_1) + n\left(\frac{\partial V}{\partial x_1}\right)_{T,p}\left(\frac{\partial x_1}{\partial n_1}\right)_{T,p,n_2}$$

$$= V + (1-x_1)\left(\frac{\partial V}{\partial x_1}\right)_{T,p} \qquad (4.36a)$$

(where $x_1 = n_1/(n_1+n_2)$)

$$\bar{V}_2\ (T,p,x_1) = \left(\frac{\partial V}{\partial n_2}\right)_{T,p,n_1}$$

$$= V\ (T,p,n_1) + n\left(\frac{\partial V}{\partial x_1}\right)_{T,p}\left(\frac{\partial x_1}{\partial n_1}\right)_{T,p,n_2}$$

$$= V - x_1\left(\frac{\partial V}{\partial x_1}\right)_{T,p} \qquad (4.36b)$$

One could expand this definition to as many components as one wished. The resulting partial molar volume would be

$$\bar{V}_j(T,p,\{n_i\}) = V + \sum_i(\delta_{ij} - x_i)\left(\frac{\partial V}{\partial x_i}\right)_{T,p,x_{k\neq i}}$$

where, δ_{ij} is the Kronecker delta ($\delta_{ij}=1$ when $i=j$ and $\delta_{ij}=0$ when $i\neq j$), and x_i is the set of independent mole fractions. Recall that the number with independent mole fractions is one fewer than the number of components since the sum of the mole fractions is unity.

Figure 4.1 shows the molar volume plotted versus mole fraction for a binary mixture. Eqns 4.36a and b have an immediate geometric interpretation; $\bar{V}_1$ and $\bar{V}_2$ are respectively the $x_1=1$ and $x_1=0$ intercepts of the tangent to V at x_1. It immediately follows that

$$V = x_1\bar{V}_1 + (1 - x_1)\bar{V}_2 \tag{4.37}$$

which is consistent with the notion that the partial molar volumes are, in a sense, effective volumes for the components in the solution. If one moves to mixtures with more than two components, the partial molar volume becomes the intersection of a many dimensional plane tangent to the V-composition surface at the composition of the mixture with the respective pure component axes.

By evaluating the composition derivative of the molar volume, another important relationship can be derived.

$$\left(\frac{\partial V}{\partial x_1}\right)_{T,p} = \bar{V}_1 - \bar{V}_2 + x_1\left(\frac{\partial V_1}{\partial x_1}\right)_{T,p} + (1-x_1)\left(\frac{\partial V_2}{\partial x_1}\right)_{T,p} \tag{4.38}$$

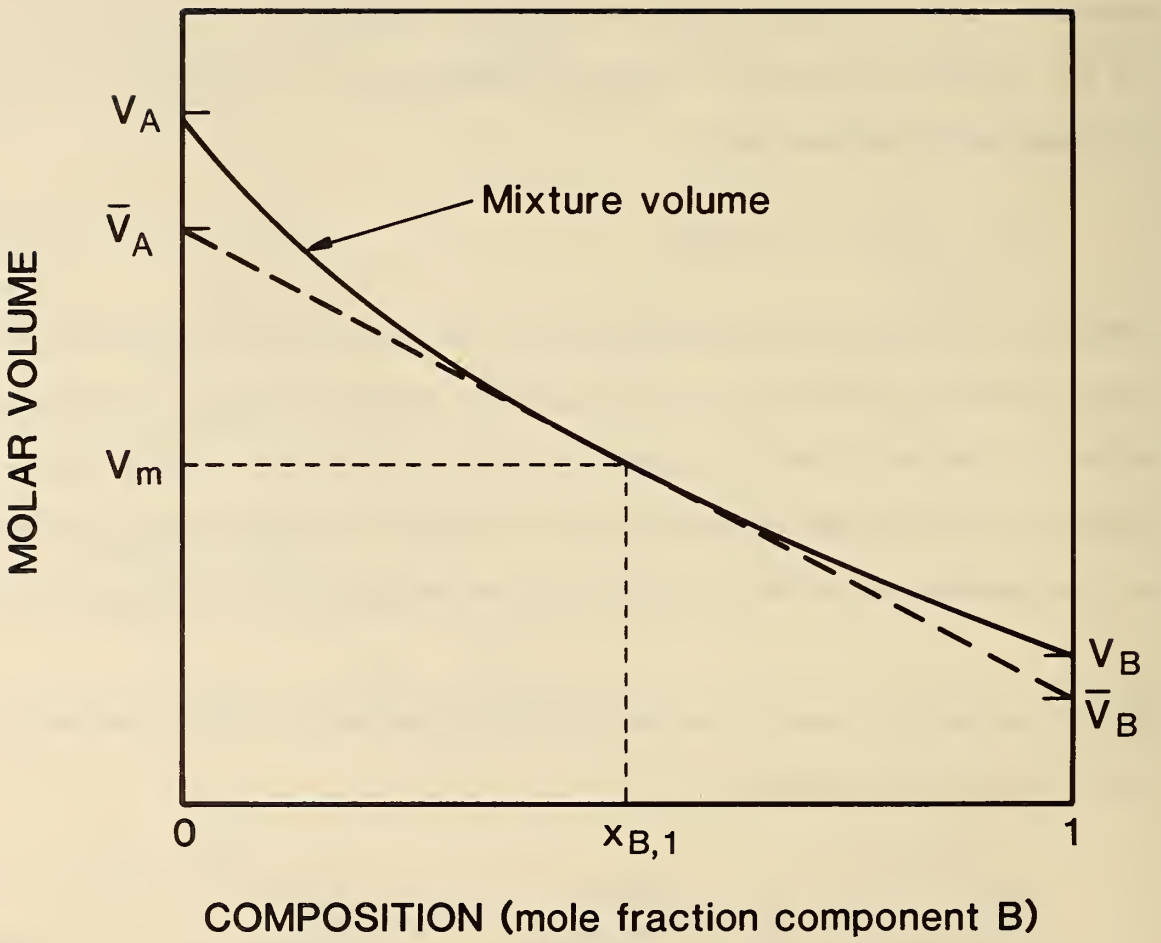

Figure 4.1. Molar volume of a mixture at a fixed temperature and pressure showing relationship between pure component and mixture molar volumes and the partial molar volumes of each component.

The difference $\bar{V}_1 - \bar{V}_2$ can be evaluated by subtracting Eqn. 4.36b from Eqn. 4.36a; however, that difference equals $\left(\frac{\partial V}{\partial X_1}\right)_{T,p}$. One concludes then that

$$x_1\left(\frac{\partial V_1}{\partial x_1}\right)_{T,p} + (1-x_1)\left(\frac{\partial V_2}{\partial x_1}\right) = 0 \tag{4.39}$$

This relation, one of a set of relations known as 'Gibbs-Duhem' relations, can be justified geometrically by noting that when the tangent is rolled along the $V - x_1$ curve that changes in the right and left intercepts are related by construction of similar triangles as follows:

$$\frac{\delta V_2}{x_1} = -\frac{\delta V_1}{1-x_1}$$

For the purposes of phase equilibrium in mixtures, the most important partial molar quantity is the chemical potential, which can be defined in the following ways:

$$\mu_A = (\partial E(S,V,\{n_i\})/\partial n_A)_{S,V,n_i \neq A}$$

$$= (\partial H(S,p(V),\{n_i\})/\partial n_A)_{S,p,n_i \neq A}$$

$$= (\partial A(T,V,\{n_i\})/\partial n_A)_{T,V,n_i \neq A}$$

$$= (\partial G(T,p(V),\{n_i\})/\partial n_A)_{T,p,n_i \neq A} \tag{4.40}$$

The chemical potential for the Carnahan-Starling-DeSantis equation of state is most easily evaluated by differentiating the Hemholtz free energy; the resulting expression is given in Table 4.1 for a binary mixture.

Whenever two or more phases are in equilibrium, not only must the temperature and pressures of all phases be the same, but also the chemical potential of each component must be equal in all phases. This result is a consequence of the thermodynamic stability requirement that, at a fixed temperature and pressure, the Gibbs free energy of a system will seek a minimum. How the phase equilibrium arises can be seen in Figure 4.2, where the molar Gibbs free energies for the two phase forms intersect at x_0; however, between x_1 and x_2, the mixture can have yet a lower Gibbs free energy by forming two phases. The free energy of the two phase system lies on the common tangent to the free energy curves for each phase form. In an argument similar to the one for the volumes, the $x_B = 0$ and $x_B = 1$ intercepts represent the respective partial molar Gibbs free energies (or chemical potentials). With the common tangent construction, one can readily see that the respective chemical potentials of each of the components will be the same in both phases. Were one dealing with a three component system, there would be a common tangent plane construction; for systems with more than three components, there would be a common tangent hyperplane, a problem that is more easily contemplated mathematically than visualized.

In this section, we have reviewed several important ideas. First, we found that the properties of the perfect gas state for both pure materials and for mixtures was an essential device for connecting one state of a material with

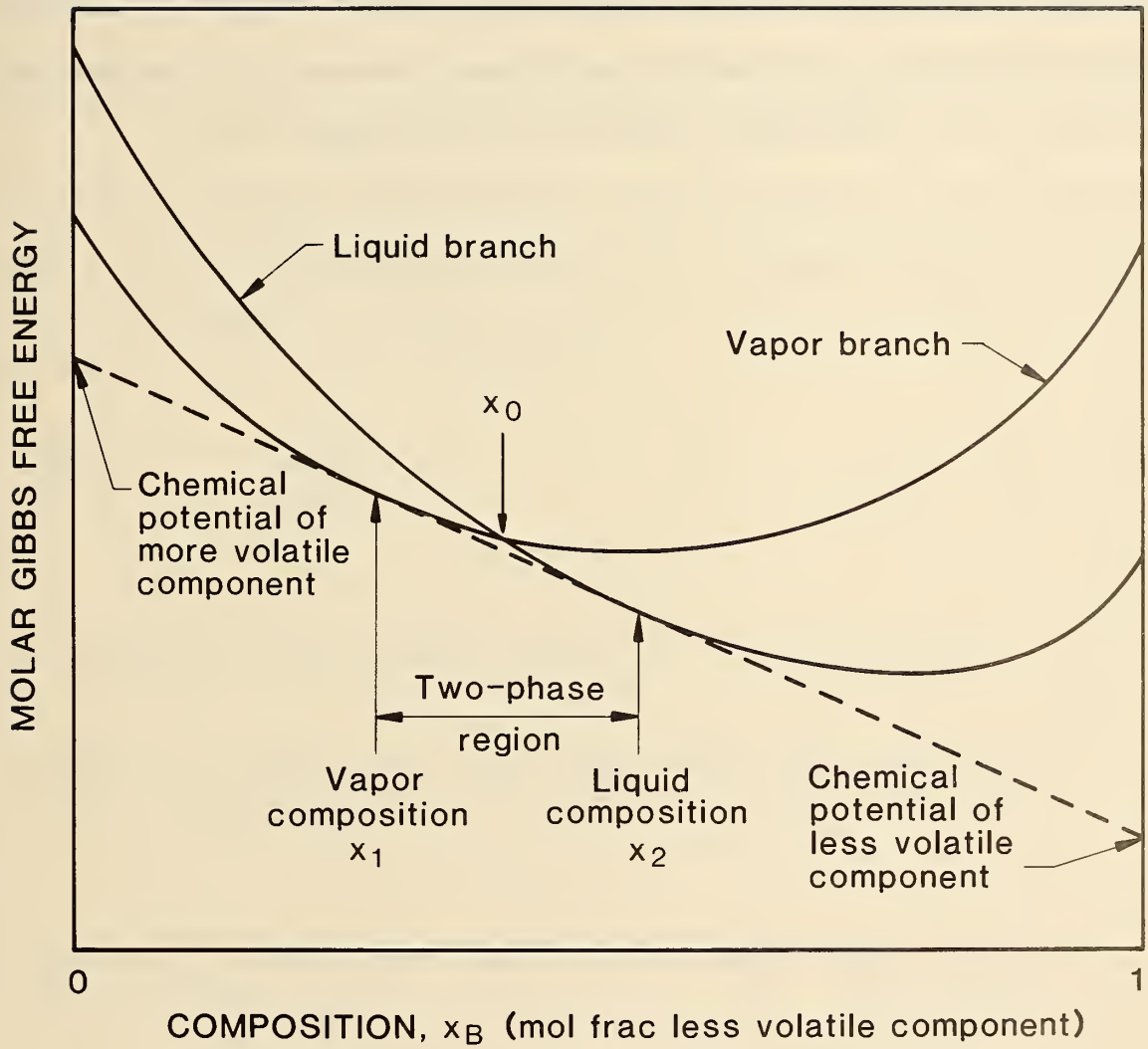

Figure 4.2 Molar Gibbs free energy of a mixture at a fixed temperature and pressure. The stable phase is the one having the lower Gibbs free energy; for compositions lying between a common tangent to the liquid and vapor branches a two-phase mixture posses a lower free energy than either phase.

another. Second, we found that the p-V-T equation of state alone was not adequate to describe the temperature dependence of a material; knowledge of the perfect gas heat capacities was essential. Finally, we found that the properties of a mixture could be connected to the properties of its constituent components through the ideal-perfect gas mixture and that, by using this device, the reference states of the constituent components of a mixture define the values of the thermodymamic properties of the mixture itself.

5. CRITICAL BEHAVIOR AND THE EFFECT OF NEARBY CRITICAL POINTS

Through the past few sections, we have developed a fluid model based upon a hard sphere reference fluid. By using this model, the thermodynamic properties of fluids, both pure components and mixtures, can be described by having only a modest set of experimental information. In this development we have avoided critical points, one phenomenon that cannot be described quantitatively by this or any of the commonly used industrial equations of state.

First, let us note that this model has a critical point. A single component fluid is at its critical point when the first and second derivatives of pressure with respect to volume are zero:

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \qquad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \tag{5.1}$$

For the Carnahan-Starling-DeSantis equation of state this yields:

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 = \frac{RT}{V^2\left(V - \frac{b}{4}\right)^4}\left[-V^4 - bV^3 - \frac{b^2V^2}{4} + \frac{b^3V}{16} - \frac{b^4}{256}\right] + \frac{a(2V + b)}{V^2(V + b)^2} \tag{5.2}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 = \frac{RT}{V^3\left(V - \frac{b}{4}\right)^5}\left[2V^5 + \frac{7bV^4}{2} + \frac{5b^2V^3}{4} - \frac{5b^3V^2}{16} + \frac{5b^4V}{128} - \frac{b^5}{512}\right]$$

$$+ \frac{a(-6V^2 - 6Vb - 2b^2)}{V^3(V + b)^3} \tag{5.3}$$

where all quantities are evaluated at the critical point.

Equations (5.2) and (5.3) could in principle be solved to yield the critical temperature and volume in terms of the a and b parameters; the critical pressure would then be given directly by the equation of state. The complexity of these expressions, however, makes an analytical solution impossible. Thus we postulate:

$$V_c = \lambda_1 b_c \tag{5.4}$$

where λ_1 is a constant. Such a relationship holds for the van der Waals-like equations of state. Substitution of Eqn. (5.4) into Eqn. (5.2) yields for the critical temperature:

$$T_c = \frac{a_c \lambda_2}{RV_c} = \frac{a_c \lambda_2}{R\lambda_1 b_c} \tag{5.5}$$

where λ_2 is a complex function of λ_1 and thus also a constant. Equation (5.3) is satisfied using the above expressions for V_c and T_c, thus confirming the assumed relationship for V_c (Eqn. 5.4). A numerical solution of the above system of equations yields:

$$V_c = 3.006818\ b_c \tag{5.6}$$

$$T_c = \frac{0.227329 a_c}{Rb_c} \tag{5.7}$$

The critical pressure is given by:

$$p_c = \frac{0.315714\ RT_c}{V_c} \tag{5.8}$$

The constant 0.316 in Eqn. (5.8) is the value of the compressibility factor at the critical point. This compares to a critical compressibility of 0.375 for the van der Waals equation and 1/3 for the Redlich-Kwong-Soave equation of state. A wide variety of organic fluids have a Z_c of approximately 0.27-0.29 (Reid, et al., 1977), thus none of these equations of state can quantitatively predict near critical behavior. Were we to use data far from the critical point (Sengers et al., 1981) to evaluate the parameters in the equation, we would find the following discrepencies between the measured and predicted critical properties: first, the predicted and measured critical points would not coincide within experimental uncertainty; second, the predicted values of all the extensive properties--volumes, enthalpies, entropies, etc.--would differ from the measured values in fundamental ways; finally, the values of the thermodynamic response functions--heat capacities at both constant pressure and volume, the isothermal compressibility, and the thermal expansion coefficient--would all diverge more strongly near the critical point than those respective properties predicted by the equation of state.

One is tempted to resolve these differences by forcing the equation of state to match the critical behavior. Such coercion does not represent an acceptable solution to what is a fundamental physical problem. Forcing the equation of state to match the critical behavior affects the temperature dependence of the molecular parameters a and b; thus, states far from the critical density--and critical point--but near the critical temperature would 'sense' the critical point in a physically unrealistic way. The alteration of

an equation of state to produce both proper near-critical and far-from-critical behavior is a major task (Woolley, 1983) (Fox, 1983) and will not be discussed here. As long as one is not operating too near the critical point, a somewhat subjective criteria that depends upon the property being considered, 'classical' equations of state, such as the one discussed in this paper, can describe the properties of a fluid quite accurately.

The criteria for critical points in binary mixtures are the following:

$$D = \begin{vmatrix} \left(\frac{\partial^2 A}{\partial V^2}\right)_{T,x} & \left(\frac{\partial^2 A}{\partial x \partial V}\right)_T \\ \left(\frac{\partial^2 A}{\partial x \partial V}\right)_T & \left(\frac{\partial^2 A}{\partial x^2}\right)_{V,T} \end{vmatrix} = 0 \tag{5.9a}$$

and

$$D^* = \begin{vmatrix} \left(\frac{\partial D}{\partial V}\right)_{T,x} & \left(\frac{\partial^2 A}{\partial x \partial V}\right)_T \\ \left(\frac{\partial D}{\partial x}\right)_{T,V} & \left(\frac{\partial^2 A}{\partial x^2}\right)_{V,T} \end{vmatrix} = 0 \tag{5.9b}$$

or, by straightforward thermodynamic transformation

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{T,p} = 0 \text{ and } \left(\frac{\partial^3 G}{\partial x^3}\right)_{T,p} = 0 \tag{5.10}$$

Although the criteria for mixtures appear to be different than for pure materials, the physical and thermodynamic reasons for them are the same. The differences are only the consequences of the additional degrees of freedom, the compositions, available in mixtures and not in pure materials. Indeed, the pure material criteria expressed in Eqn. 5.1, are a special case of the criteria in Eqn. 5.9a and b. The essence of Eqns. 5.1, 5.9a and 5.9b is the thermodynamic stability requirement arising from the second law; for a system to be stable any perturbation of the system at fixed volume and temperature must cause the Helmholtz free energy to rise. The first of the criteria in Eqn. 5.1 and that in Eqn. 5.9a define the boundary between a locally stable and unstable thermodynamic state. A critical point is a special place on this boundary that requires that any perturbation will lead into a stable state; at other points on the boundary there will be perturbations that lead into unstable states. The important fact to note however is that the critical point for a mixture is not given by the same function of a and b as the pure materials.

Even though the equation of state cannot quantitatively predict the near critical region, applying such an expression to mixtures is superior to the usual mixing rules. The simplest mixture approximation, and one that is often applied, is that of an ideal mixture where the mixture property (e.g., molar volume) is given by the mole fraction weighted average of the pure component values:

$$V_m = x_A V_A + x_B V_B \tag{5.11}$$

Such mixing rules can work well when both pure components are well below or above their critical points and if no strong intermolecular interactions (such as hydrogen bonding) are present. These rules can collapse, however, when one of the components is near its critical point, even though the mixture itself may be an ordinary fluid (Morrison, 1985).

Figure 5.1 shows how errors can arise with simple mixing rules. In this illustration, which plots molar liquid volume against composition, the temperature is near, but below, the critical temperature of component A and well below the critical temperature of component B in the representative mixture A/B. The curve ab is the locus of saturated liquid volumes. The curve af is the isobar at the saturation pressure of component A. The strong curvature of ab and af near the pure A side of the figure are indicative of the near critical state of component A. The ideal mixture approximation would give a straight line between a and b or, more correctly between a and f. In both cases, the straight line deviates from the corresponding curves by about 15 percent in the mid composition range for this example. Of course, by the nature of the mixing rule, the curve and line must coincide at pure A and B. A well-chosen equation of state, however, would follow the proper curved path, although perhaps deviating from the actual volume as the mixture approaches its critical point at high concentrations of A.

In summary, so long as one stays away from the critical point of the mixture, classical equations of state can be made to work quite adequately for the quantitative evaluation of the properties of the mixture. As noted before, one's only recourse should one of the components of this mixture be near to or

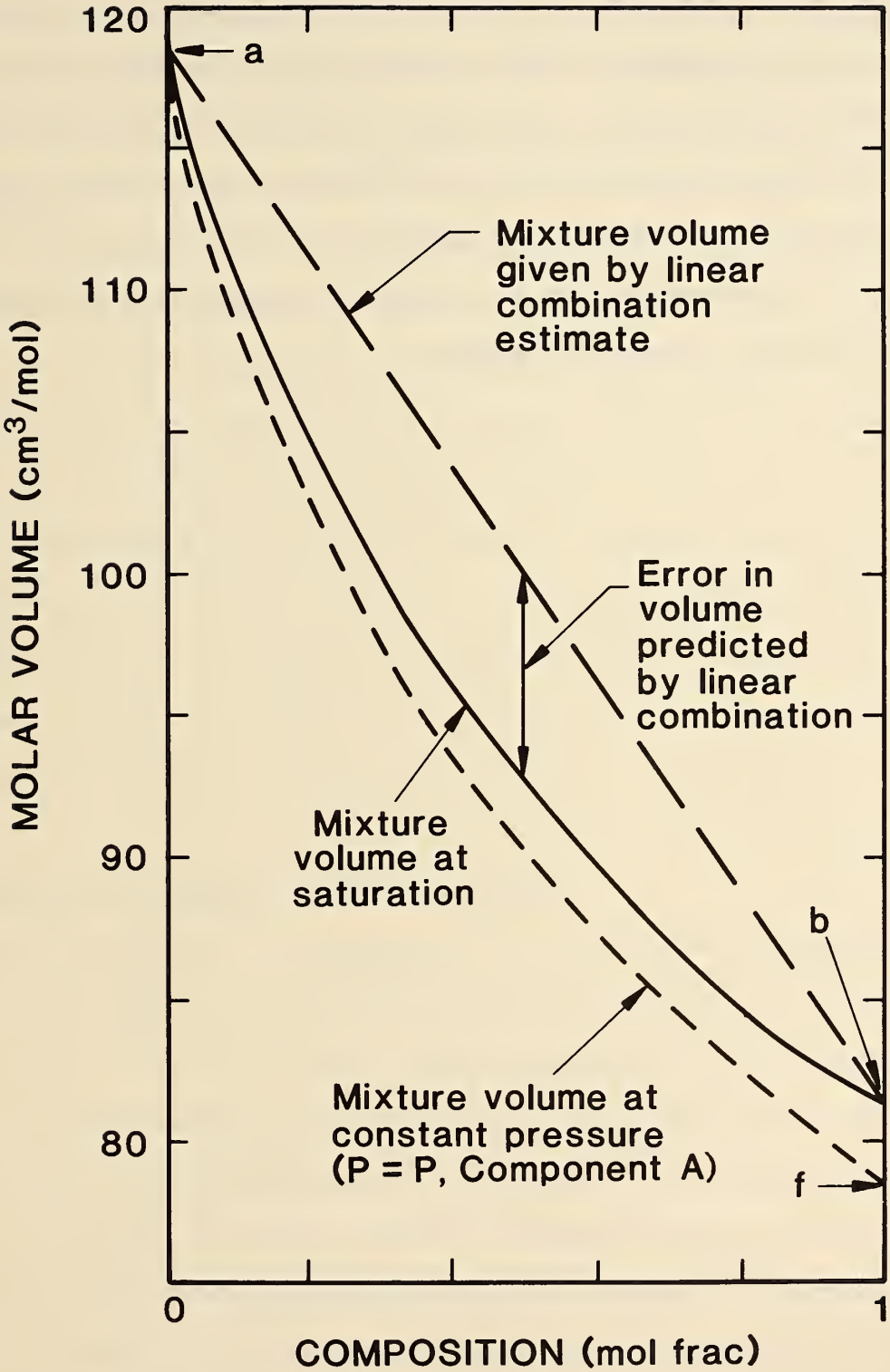

Figure 5.1. Molar volume of a mixture at a fixed temperature showing error of estimating mixture properties by a linear combination of the pure component values.

above its critical point is the use of an equation of state; all schemes used for ordinary liquids break down completely under such conditions. As indicated previously, the problem is more fundamental than the absence of liquid data for the respective component above its critical point; the presence of a nearby critical point causes properties that otherwise change slowly and smoothly with changes in composition, temperature, or pressure, to change rapidly. As a consequence any linear interpolation scheme ceases to serve as a quantitative way of estimating a property.

6. NUMERICAL IMPLEMENTATION

The algorithms which express the p-V-T and thermodynamic relationships presented in the preceeding sections have been implemented in a set of computer subroutines written in standard ASCII FORTRAN (FORTRAN 77). These are summarized in Table 6.1 and fall into four general categories: 1) subroutines to determine the a and b parameters and the mixing coefficient, f, from saturation data, 2) routines which store coefficients for the a, b and C_p^o expressions for pure components and calculate these parameters as a function of temperature and composition for a mixture, 3) property routines for the calculation of enthalpy, heat capacity, entropy, specific volume, and saturation pressure and 4) auxiliary routines which are referenced by the other property routines. The subroutines are interdependent with one calling another. This section details the methods of solution employed by these routines. The required inputs and resulting outputs for each routine are summarized in Table 6.1 and discussed in detail in Appendix B.

Determination of Equation of State Parameters

The a and b parameters in the equation of state must be determined as a function of temperature for each of the pure materials of interest. Data are required for this determination. Laboratory measurements or original literature values are preferable; tabular values (e.g., from handbooks) may also be used but are less desirable because considerable data smoothing has taken place to generate the tables. The most commonly available and generally most reliable vapor-liquid equilibria data are the saturated liquid and vapor specific volumes and the equilibrium vapor pressure at a given temperature. The present algorithm is developed for these data although the overall methodology is general and can be modified to accomodate other data.

Table 6.1. Summary of Thermodynamic Property and Associated Subroutines

Name	Description/Inputs/Outputs	Other Routines Called
Data Fitting Routines		
FITAB	determine pure component a,b parameters inputs: T, $p_{sat,e}$, $V_{\ell,e}$, V_{ve}, ω_p, ω_ℓ, ω_v outputs: a,b	PLIMIT, VIT
FITF	determine interaction parameters from mixture data inputs: T, x_ℓ, some combination of: $p_{sat,e}$, $V_{\ell,e}$, $V_{v,e}$, $x_{v,e}$ output: f_{12}	BCONST, BUBLT, ENTROP ESPAR, HCVCP, PLIMIT, VIT, ZXLSF
Routine to Access Stored Parameters		
BCONST	access eqn state parameters from data base and calculate reference states for H,S inputs: code nos. for pure comp., f_0, f_1 outputs: (contained in common blocks) note: must be referenced once for each mixture before calling any of following routines.	BDESC (via common blocks), BUBLT, ENTROP, ESPAR, HCVCP, PLIMIT, VIT
Property Routines		
BUBLT	calculate bubble or dew point pressure inputs: T, x of parent phase outputs: P, x of incipient phase, V_ℓ, V_v	ESPAR, PLIMIT, VIT
ENTROP	compute specific entropy inputs: T, V, x output: S (returned as function value)	ESPAR
HCVCP	compute enthalpy and/or heat capacity inputs: T, V, x, IQ - output qualifier outputs: H and/or C_v and/or C_p (as specified by IQ)	ESPAR

Auxiliary Routines (transparent to user but required in executable element):

BDESC	Block data routine containing pure component data
ESPAR	compute a, b, C_p^o, f_{12} as functions of T,x from stored coefficients
PLIMIT	find upper and lower bounds on pressure given T
VIT	specific volume for liquid or vapor as function of T,p
ZXLSF	or equivalent one-dimensional minimization routine from math/statistics library (required only with FITF)

Pressure and liquid and vapor volume are more than sufficient to determine 'a' and 'b' and thus the parameters are chosen to minimize the following sum of squares:

$$\Gamma(a,b,T) = \omega_\ell\left(\frac{V_{\ell,e} - V_{\ell,c}}{V_{\ell,e}}\right)^2 + \omega_v\left(\frac{V_{v,e} - V_{v,c}}{V_{v,e}}\right)^2 + \omega_p\left(\frac{p_{sat,e} - p_{sat,c}}{p_{sat,e}}\right)^2 \qquad (6.1)$$

where the e and c subscripts refer to experimental data and calculated values respectively and the ω terms are weighting factors which can be adjusted to match the reliability of the various measured quantities. The calculated pressure and volumes are evaluated using the equation of state subject to the constraint that the Gibbs free energy of the liquid and vapor phases be equal.

The function Γ is at a minimum where the partial derivatives with respect to 'a' and 'b' are zero:

$$\frac{\partial\Gamma}{\partial a} = 0 = \omega_\ell\left(\frac{V_{\ell,e} - V_{\ell,c}}{V^2_{\ell,e}}\right)\frac{\partial V_{\ell,c}}{\partial a} + \omega_v\left(\frac{V_{v,e} - V_{v,c}}{V^2_{v,e}}\right)\frac{\partial V_{v,c}}{\partial a}$$

$$+ \omega_p\left(\frac{p_{sat,e} - p_{sat,c}}{p^2_{sat,e}}\right)\frac{\partial p_{sat,c}}{\partial a} \qquad (6.2)$$

$$\frac{\partial\Gamma}{\partial b} = 0 = \omega_\ell\left(\frac{V_{\ell,e} - V_{\ell,c}}{V^2_{\ell,e}}\right)\frac{\partial V_{\ell,c}}{\partial b} + \omega_v\left(\frac{V_{v,e} - V_{v,c}}{V^2_{v,e}}\right)\frac{\partial V_{v,c}}{\partial b}$$

$$+ \omega_p\left(\frac{p_{sat,e} - p_{sat,c}}{p^2_{sat,e}}\right)\frac{\partial p_{sat,c}}{\partial b} \qquad (6.3)$$

Because the equation of state is fifth order in volume, Equations 6.3 and 6.4 cannot be solved explicitly. To set up an iteration in a and b the calculated

quantities resulting from small changes in a and b (δa and δb) are expanded in terms of partial derivatives; for example:

$$V_{\ell,c}(a + \delta a, b + \delta b, T) = V_{\ell,c}(a,b,T) + \frac{\partial V_{\ell,c}(a,b,T)}{\partial a}\,\delta a + \frac{\partial V_{\ell,c}(a,b,T)}{\partial b}\,\delta b \qquad (6.4)$$

The combination of equations 6.2 and 6.3 with equation 6.4 and similar expressions for $V_{v,c}$ and $P_{sat,c}$ yields:

$$\left[\frac{\omega_\ell}{V^2_{\ell,e}}\left(\frac{\partial V_{\ell,c}}{\partial a}\right)^2 + \frac{\omega_v}{V^2_{v,e}}\left(\frac{\partial V_{v,c}}{\partial a}\right)^2 + \frac{\omega_p}{p^2_{sat,c}}\left(\frac{\partial p_{sat,c}}{\partial a}\right)^2\right]\delta a +$$

$$\left[\frac{\omega_\ell}{V^2_{\ell,e}}\frac{\partial V_{\ell,c}}{\partial a}\frac{\partial V_{\ell,c}}{\partial b} + \frac{\omega_v}{V^2_{v,e}}\frac{\partial V_{v,c}}{\partial a}\frac{\partial V_{v,c}}{\partial b} + \frac{\omega_p}{p^2_{sat,e}}\frac{\partial p_{sat,c}}{\partial a}\frac{\partial p_{sat,c}}{\partial b}\right]\delta b$$

$$= \omega_\ell\left(\frac{V_{\ell,e} - V_{\ell,c}}{V_{\ell,e}^{\,2}}\right)\frac{\partial V_{\ell,c}}{\partial a} + \omega_v\left(\frac{V_{v,e} - V_{v,c}}{V^2_{v,e}}\right)\frac{\partial V_{v,c}}{\partial a} +$$

$$\omega_p\left(\frac{p_{sat,e} - p_{sat,c}}{p^2_{sat,e}}\right)\frac{\partial p_{sat,c}}{\partial a} \qquad (6.5)$$

$$\left[\frac{\omega_\ell}{V^2_{\ell,e}}\frac{\partial V_{\ell,c}}{\partial b}\frac{\partial V_{\ell,c}}{\partial a} + \frac{\omega_v}{V^2_{v,e}}\frac{\partial V_{v,c}}{\partial b}\frac{\partial V_{v,c}}{\partial a} + \frac{\omega_p}{p^2_{sat,e}}\frac{\partial p_{sat,c}}{\partial b}\right]\delta a +$$

$$\left[\frac{\omega_\ell}{V^2_{\ell,e}}\left(\frac{\partial V_{\ell,c}}{\partial b}\right)^2 + \frac{\omega_v}{V^2_{v,e}}\left(\frac{\partial V_{v,c}}{\partial b}\right)^2 + \frac{\omega_p}{p^2_{sat,e}}\left(\frac{\partial p_{sat,c}}{\partial b}\right)^2\right]\delta b$$

(Continued on next page)

$$= \omega_\ell \left(\frac{V_{\ell,e} - V_{\ell,c}}{V_{\ell,e}^2} \right) \frac{\partial V_{\ell,c}}{\partial b} + \omega_v \left(\frac{V_{v,e} - V_{v,c}}{V_{v,e}^2} \right) \frac{\partial V_{v,c}}{\partial b} +$$

$$\omega_p \left(\frac{p_{sat,e} - p_{sat,c}}{p_{sat,e}^2} \right) \frac{\partial p_{sat,c}}{\partial a} \tag{6.6}$$

where all quantities are evaluated at (a,b). The partial derivatives are approximated numerically, for example:

$$\frac{\partial V_{\ell,c}}{\partial a} \cong \frac{V_\ell(a + \Delta a, b) - V_\ell(a,b)}{\Delta a} \tag{6.7}$$

$$\frac{\partial V_{\ell,c}}{\partial b} \cong \frac{V_\ell(a, b + \Delta b) - V_\ell(a,b)}{\Delta b} \tag{6.8}$$

Equations 6.5 and 6.6 form a linear system in δa and δb. Given starting values of a and b the system can be solved to give improved guesses:

$$a^{(i+1)} = a^{(i)} + \delta a \tag{6.9}$$

$$b^{(i+1)} = b^{(i)} + \delta b \tag{6.10}$$

where the subscript is the iteration index.

In the implementation of the above method, the routine FITAB generates starting guesses of a and b using the saturated volume data alone. Starting at $b = 1/2\ V_{\ell,e}$ the value of the a parameter is expressed in terms of b by equating the pressure of the liquid and vapor:

$$a = \frac{\dfrac{RT(1 + y_\ell + y_\ell^2 - y_\ell^3)}{V_{\ell,e}(1 - y_\ell)^3} - \dfrac{RT(1 + y_v + y_v^2 - y_v^3)}{V_{v,e}(1 - y_v)^3}}{\dfrac{1}{V_\ell(V_\ell + b)} - \dfrac{1}{V_v(V_v + b)}} \tag{6.11}$$

where:

$$y_\ell = \frac{b}{4V_{\ell,e}} \quad ; \quad y_v = \frac{b}{4V_{v,e}}$$

A Newton's method iteration is carried out to find the value of b which satisfies:

$$\Psi(b) = 0 = G_\ell(a,b,T,V_{\ell,e}) - G_v(a,b,T,V_{v,e}) \tag{6.12}$$

If only specific volume data were available this iteration could be used to determine a and b.

With the above starting values for a and b the iteration outlined in eqns. 6.5 to 6.10 is then carried out by FITAB. For each guess of (a,b) an inner iterative loop is used to calculate the pressure and liquid and vapor volume. This iteration is based on the equality of the liquid and vapor Gibbs free energy and is identical to the one used in the BUBLT routine discussed below. The iteration is repeated at $(a + \Delta a, b)$ and $(a, b + \Delta b)$ in order to evaluate the partial derivatives (where $\Delta a = 0.001\ a$ and $\Delta b = 0.001\ b$). The system of equations 6.5 and 6.6 is then evaluated and solved for δa and δb to generate a new (a,b) by eqns. 6.9, 6.10. The iteration is repeated until 'a' and 'b' are determined to a specified accuracy.

The a and b determined for individual data sets are then fit to simple functions of temperature (such as eqns. 6.14, 6.15) to arrive at the final expressions required by the property routines. Users are warned that because the FITAB routine assumes saturation data it cannot be used at or above the critical point. Furthermore, attempts to force the equation of state to fit liquid-vapor equilibrium data near the critical point (i.e., at a reduced temperature above about 0.95) will cause a degradation in accuracy for points near the critical temperature but removed from the critical region. This effect occurs with any equation of state that arises from the so-called mean field approximation. This class includes all industrial equations of state.

The subroutine FITAB computes the a and b parameters at a single temperature from saturation data at that temperature. If the various saturation quantities are not all measured at the same temperature or if superheated vapor data is to be used in computing a and b, the subroutine FITAB cannot be used, rather it is necessary to carry out a non-linear least squares regression of the entire experimental data set. Non-linear regression routines are commonly available in statistics libraries but because they, as well as the data to be fit, vary widely in form only a general discussion of using such a routine is given here. A regression routine would find the set of parameters that minimizes the sum of squares of residuals between the experimental data points and corresponding calculated values. Typically, an external subroutine computes the residuals as a function of the parameters to be optimized (e.g., a_0, a_1, a_2, b_0, b_1, b_2 in eqns. 6.14 and 6.15). The process is iterative and generally requires reasonably good initial guesses for the parameters. For each set of parameter estimates generated by the iteration in the regression program the external model subroutine is called to compute a

revised set of residuals. This external subroutine must therefore update the common block containing the a_i and b_i coefficients and call the routine BCONST (which computes reference state values as described below) before computing the residuals with BUBLT or similar routines.

Determination of Interaction Parameter

The mixing rule for the 'a' parameter for a mixture involves the interaction parameter, f_{12}, which must be determined from experimental data. The approach is again to find the value of f_{12} which minimizes the sum of squares of relative deviations between measured and calculated quantities:

$$\Gamma(T, x_\ell, f_{12}) = \omega_p \left(\frac{p_{sat,e} - p_{sat,c}}{p_{sat,e}}\right)^2 + \omega_\ell \left(\frac{V_{\ell,e} + V_{\ell,c}}{V_{\ell,e}}\right)^2 + \omega_v \left(\frac{V_{v,e} + V_{v,c}}{V_{v,e}}\right)^2$$

$$+ \omega_x \, (x_{v,e} - x_{v,c})^2 \qquad (6.13)$$

Because the vapor composition must be between zero and unity, the last term in eqn. 6.13 is expressed as an absolute error. Only a single measured quantity in addition to T and x_ℓ is necessary to determine f_{12}. If all of the data indicated in eqn. 6.13 is not available, the corresponding weighting factors in the expression for Γ are set to zero.

The subroutine FITF will accept any combination of P_{sat}, V_ℓ, V_v and x_v data but requires the a and b parameters for the pure components (i.e., pure component data in the BDESC routine described below). For given values of T and x_ℓ and the current iterative value of f_{12}, the BUBLT subroutine (discussed below) is used to provide the calculated pressure, volumes and vapor

composition needed to compute eqn. 6.13. The actual minimization is carried out by the subroutine ZXLSF contained in the proprietary IMSL library accessed through the NBS central computer. It is expected that users will have access to a similar one-dimensional minimization routine and can modify the appropriate lines of FITF.

The values of f_{12} calculated for different individual data sets should be constant, or at most a function of temperature, for a given pair of pure components. A wide variation in f_{12} with composition indicates either poor mixture data or an inability of the equation of state to represent the entire composition range of the mixture. In the latter case, the user must choose a value of f_{12} consistent with the composition range of interest. The values of f_{12} determined near the pure component compositions typically will have greater uncertainty than values determined in the middle of the composition range.

Calculation of Equation of State Parameters from Stored Coefficients

The coefficients of the curve fits to the parameters a, b and C_p^o for 11 pure refrigerants are stored in common blocks initialized in the BLOCK DATA element BDESC. This element also contains molecular weights, critical properties, reference state conditions for enthalpy and entropy and character variable representations of the refrigerant names. The refrigerants currently in the data base are listed in Table 6.2. The data arrays are dimensioned for 20 components so that users can add data for other pure materials.

The information in BDESC for the particular refrigerant pair of interest is accessed by the subroutine BCONST and stored in subsidiary common blocks which are referenced as needed by other subroutines. The enthalpy and entropy

Table 6.2. Refrigerants Currently Included in Data Base

Code No.	ASHRAE Designation	Chemical Formula
1	R11	trichlorofluoromethane
2	R12	dichlorodifluoromethane
3	R13	chlorotrifluoromethane
4	R13B1	bromotrifluoromethane
5	R14	tetrafluoromethane
6	R22	chlorodifluoromethane
7	R23	trifluoromethane
8	R113	1,1,2-trichlorotrifluroethane
9	R114	1,2-dichlorotetrafluoroethane
10	R142b	1-chloro-1,1-difluoroethane
11	R152a	1,1-difluoroethane

routines are called at the reference temperatures of each component to establish reference values of H and S. The inputs to BCONST consist of the code numbers for the pure components (as listed in Table 6.2) and the interaction coefficient for the mixture (expressed in terms of f_0 and f_1 as given in eqn. 6.17). For a pure component the code numbers will be identical and f_0 and f_1 should be specified as zero. It is necessary to call BCONST only once (before any other property routines are referenced) for each pair of pure components considered.

The thermodynamic property routines reference the subroutine ESPAR when it is necessary to calculate the a and b parameters as a function of temperature and composition. When called by the enthalpy, entropy or heat capacity routines the C_p^o for the pure components and the temperature derivatives of a and b are also calculated. This arrangement completely isolates in ESPAR the temperature and composition dependence of the equation of state parameters except for the Gibbs free energy and chemical potential statements in BUBLT. Thus, alternative temperature dependencies or mixing rules can be accommodated by changing only two subroutines (plus of course the corresponding data in BDESC).

As presented in Appendix B the ESPAR routine calculates the a and b parameters as:

$$a = a_0 \exp(a_1 T + a_2 T^2) \tag{6.14}$$

$$b = b_0 + b_1 T + b_2 T^2 \tag{6.15}$$

The ideal gas heat capacity is represented as:

$$C_p^o = c_0 + c_1 T + c_2 T^2 \tag{6.16}$$

The interaction parameter is expressed as:

$$f_{12} = f_0 + f_1 T \tag{6.17}$$

For mixtures with an interaction parameter independent of temperature, f_1 is set to zero.

Values for the a_i, b_i and c_i are tabulated in Appendix A for 11 refrigerants. The value of the interaction parameter, f_{12}, for several mixtures for which p-V-T-x data are available are also given in Appendix A.

Dew and Bubble Point Pressures

The hard sphere equation of state represents the p-V-T behavior as an explicit expression for pressure in terms of specific volume and temperature. The application of the equation of state for a pure component, however, often requires saturation pressure as a function of temperature alone. For a mixture the bubble or dew point pressure is a function of temperature and the composition of the appropriate phase as well. This calculation is carried out by the subroutine BUBLT: given the temperature of a mixture (or pure component) and the composition of one phase this routine calculates the saturation pressure, the composition of the other phase, and the specific volume of each phase.

Vapor-liquid equilibria becomes meaningless, of course, above the critical temperature and BUBLT returns a warning message without carrying out any calculations when the temperature approaches the critical temperature. For pure components, a warning is returned at temperatures greater than 0.99 of the critical temperature predicted by eqn. 5.7. For mixtures the limit is 0.99 of the critical temperature of a hypothetical pure material having the same a(T) and b(T) as the mixture. The critical temperature of a mixture is always higher than that of the corresponding pseudo-pure material and thus, BUBLT will return a message of 'critical point exceeded' for temperatures which may be significantly below the mixture critical temperature. This limit does not arise from the equation of state itself, but results from a failure of the solution logic above the pseudo-pure material critical point. An alternate version of BUBLT which allows computation to the mixture critical point is under development.

All physically meaningful solutions to the equation of state must have a negative slope of pressure with respect to volume. Furthermore, for there to be both liquid and vapor solutions for a <u>pure</u> component the pressure will lie between the limits where $(\partial p/\partial V)_T = 0$. These limits are a function of temperature and are indicated as p_{low} and p_{up} in Figure 6.1. The slope of $\partial p/\partial V$ was given by eqn. 5.2 and is repeated here:

$$\left(\frac{\partial p}{\partial V}\right)_T = \frac{RT}{V^2\left(V - \frac{b}{4}\right)^4}\left(-V^4 - bV^3 - \frac{b^2V^2}{4} + \frac{b^3V}{16} - \frac{b^4}{256}\right) + \frac{a(2V + b)}{V^2(V + b)^2} \qquad (6.18)$$

In the limit as V approaches b/4 (i.e., as the volume approaches the molecular volume) $(\partial p/\partial V)_T$ approaches negative infinity. At a volume of V = 3.007b the

slope is positive for all temperatures below the critical temperature at least for values of a and b which are reasonable for refrigerants. (The constant 3.007 is the ratio of the critical volume to $b(T_c)$.) At the other extreme, as V approaches infinity $(\partial p/\partial V)_T$ approaches zero but remains negative. Thus between the volumes of b/4 and infinity the slope $\partial p/\partial V$ must twice pass through zero, corresponding to p_{low} and p_{up}. In the critical region of a mixture the pressure is not bounded by p_{low} and p_{up} and the solution logic fails; this is the reason that BUBLT is limited by the critical temperature of the corresponding pseudo-pure material.

The pressure limits p_{low} and p_{up} are found for a given a,b and T by the auxiliary subroutine PLIMIT. Starting at V = 3.007b the volume is decreased and eqn. 6.18 evaluated until a negative slope is found. Using these limits, the bisection technique is applied to volume to find the point at which $(\partial p/\partial V)_T = 0$. The value of p_{low} is then evaluated from the volume by eqn. 2.6. If p_{low} is negative, a small positive value is used. To find the upper bound on pressure, the volume is increased from 3.007b until a negative slope is found, the bisection method is then used once more.

For a pure component, the equilibrium criteria is the equality of Gibbs free energy between the phases:

$$G_\ell(T,V_\ell) = G_v(T,V_v) \tag{6.19}$$

The specific volumes V_ℓ and V_v are in turn functions of T and p. Graphically, eqn. 6.19 is equivalent to the requirement that the areas between a line of constant pressure and the p vs V line be equal as indicated by the shaded

areas in Figure 6.1. The general method of solution is to iterate on pressure starting at the limits of p_{low} and p_{up}. For each guess of pressure, the liquid and vapor volumes are found as a function of T and p using the subroutine VIT (discussed below). The G for each phase is then computed as a function of T and V by eqn. 4.8 (except that the G^0 terms will always cancel and are thus omitted). The iteration is continued by a combination of the secant and regula-falsi methods until the computed liquid and vapor Gibbs free energies are equal to within a convergence tolerance.

The computation of saturated volumes as a function of pressure requires an iterative calculation which is contained in the subroutine VIT. Newton's method is used to iterate on volume until the pressure computed by the equation of state agrees with the input pressure. The previous converged value of V_ℓ or V_v is used as the initial guess. To speed convergence the iteration is carried out in terms of ln(V), for the vapor volume iteration the pressure is transformed into logarithmic coordinates as well. Convergence is also aided by constraining guesses of vapor volume to values greater than the critical volume, liquid volumes are constrained to lie between b/4 and V_c.

The need for finding the upper and lower bounds on the pressure iteration stems from a potential problem with solving for V(T,p). For example, if a pressure greater than p_{up} is input to the iteration for vapor volume no solution exists on the vapor branch of the p-V curve and the iteration will either fail to converge or will converge to a solution on the liquid branch. This latter case would result in apparently equal liquid and vapor volumes and consequently equal Gibbs free energies for the two phases. This would be a trivial and physically meaningless solution to eqn. 6.19. This is a problem

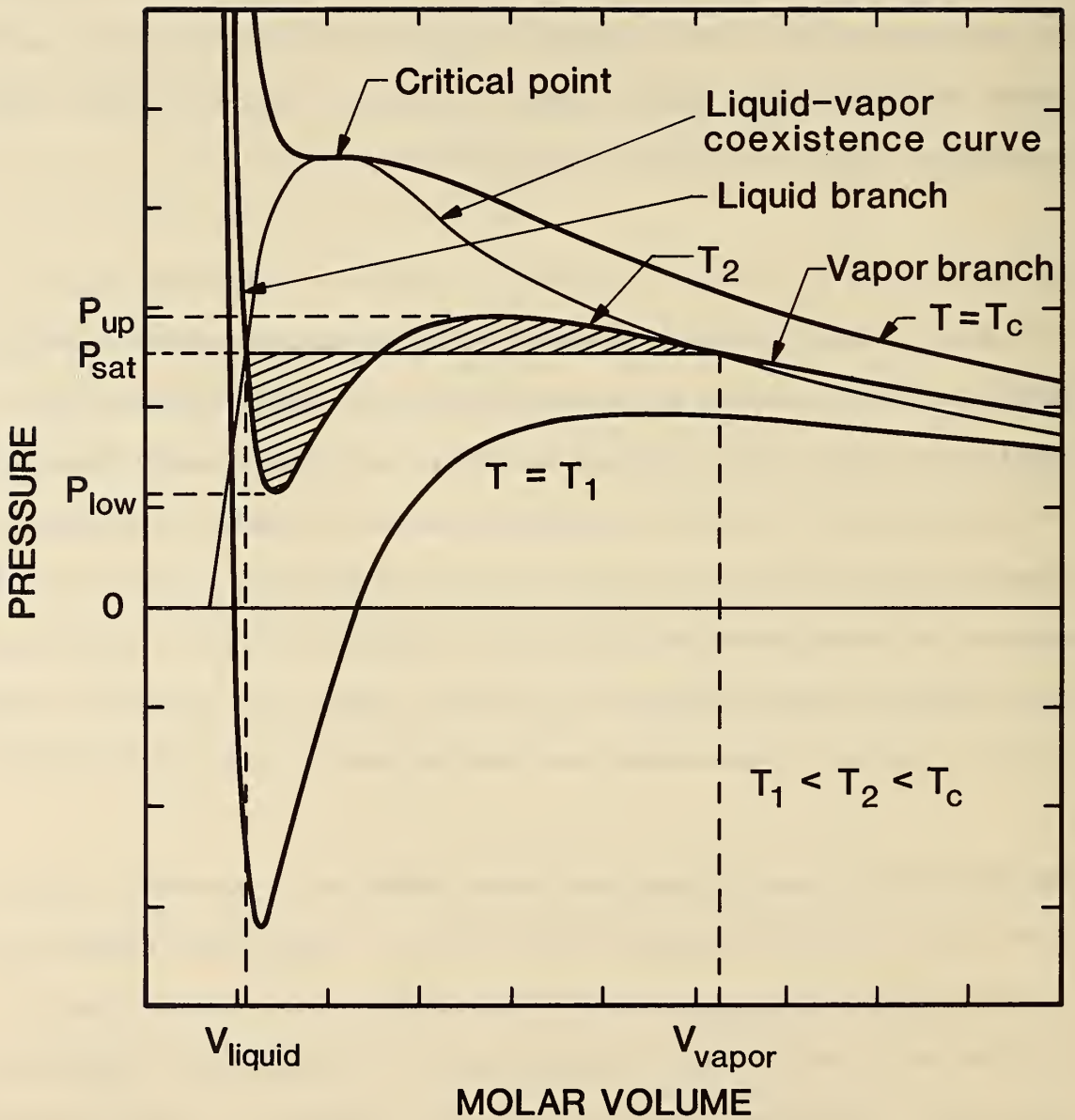

Figure 6.1. p-V-T behavior of a pure material as represented by the equation of state; vapor-liquid equilibria criteria represented by equality of shaded areas.

of the solution logic and not the equation of state itself. By bounding the pressure iteration a false solution is avoided.

For a mixture the criteria for liquid-vapor equilibrium (in addition to temperature ard pressure equality) are the equality of the chemical potential of each component in the two phases:

$$\mu_{a1}(T,x_1,V_1) = \mu_{a2}(T,x_2,V_2) \tag{6.20}$$

$$\mu_{b1}(T,x_1,V_1) = \mu_{b2}(T,x_2,V_2) \tag{6.21}$$

where the subscripts refer to components a and b in phases 1 and 2. The temperature of the mixture and the composition of the parent phase are input quantities. (The phases with the known and unknown compositions are referred to as the parent and incipient phases respectively. For a bubble point calculation the parent phase is liquid; a parent phase of vapor gives the dew point pressure.)

Two concentric iteration loops are employed in the BUBLT routine to solve for the saturation pressure and the composition of the incipient phase. For each guess of pressure the volume and chemical potentials of the parent phase are computed. The inner iteration loop for composition is entered and the incipient phase a, b, V and μ's are computed for the current guess of x_2. The chemical potentials are combined with the current guess of x_2 to yield the function used with secant/reguli-falsi iteration:

$$\Psi(x_2) = \frac{z_a}{z_a + z_b} - x_2 \tag{6.23}$$

where $z_a = x_1 \exp(\mu_{a1} - \mu_{a2})$ (6.24)

$z_b = (1 - x_1) \exp(\mu_{b1} - \mu_{b2})$ (6.25)

For each guess of pressure the composition iteration continues until $\Psi(x_2)$ is within a convergence tolerance of zero. Successive guesses of pressure in the outer iterative loop are generated by the secant/regul i-fal si method and the function:

$$\Psi(p) = 1 - (z_a + z_b) \tag{6.26}$$

This function goes to zero when the chemical potentials are equal between the phases.

The routine BUBLT applies the pure component iteration for Gibbs free energy to the mixture to calculate the saturation pressure of a pure component having the same properties as the parent phase of the mixture. This mixture is unstable with respect to two phases at this pseudo-pure component pressure and thus it represents a lower bound on pressure for a bubble point calculation and an upper bound for a dew point. The pseudo-pure component pressure is used as the starting value in the mixture iteration. The second guess for pressure (necessary to start the secant method iteration) is given by:

$$\begin{aligned} p^{(2)} &= (z_a + z_b)p^{(1)} \quad \text{(for bubble point)} \\ p^{(2)} &= p^{(1)}/(z_a + z_b) \quad \text{(for dew point)} \end{aligned} \tag{6.27}$$

To start the composition iteration an initial guess of equal parent and incipient phase compositions is made. For the second and subsequent guesses

of pressure, the x_2 iteration is started with the previous converged value of x_2. In each case the second guess value for composition is given by:

$$x_2^{(2)} = \frac{z_a}{z_a + z_b} \tag{6.28}$$

A flow chart of BUBLT is given as Figure 6.2. This routine imposes numerous checks and bounds on the calculations. Although these slow the execution time of the routine they were found to be necessary to insure reliable convergence, particularly near the critical region. BUBLT has been checked for numerous refrigerant mixtures and was found to converge quickly and reliably for a wide range of temperatures. Occasional convergence problems were encountered at very low reduced temperatures ($< 0.2\ T_c$) but this is generally well below the freezing point where the equation of state is no longer valid anyway.

Enthalpy, Heat Capacity and Entropy

The calculation of enthalpy, heat capacity and entropy are straightforward, non-iterative implementations of the expressions given in Section 4. Molar specific enthalpy and heat capacities at constant volume and pressure are computed by the subroutine HCVCP. Depending on the value of an input parameter one, two or all three of these quantities are determined as a function of temperature, composition and specific volume. The function subroutine ENTROP computes molar enthalpy by eqn. 4.49, also for a given T, x and V. The calculations for H and S employ the reference state calculated by BCONST for each pure component.

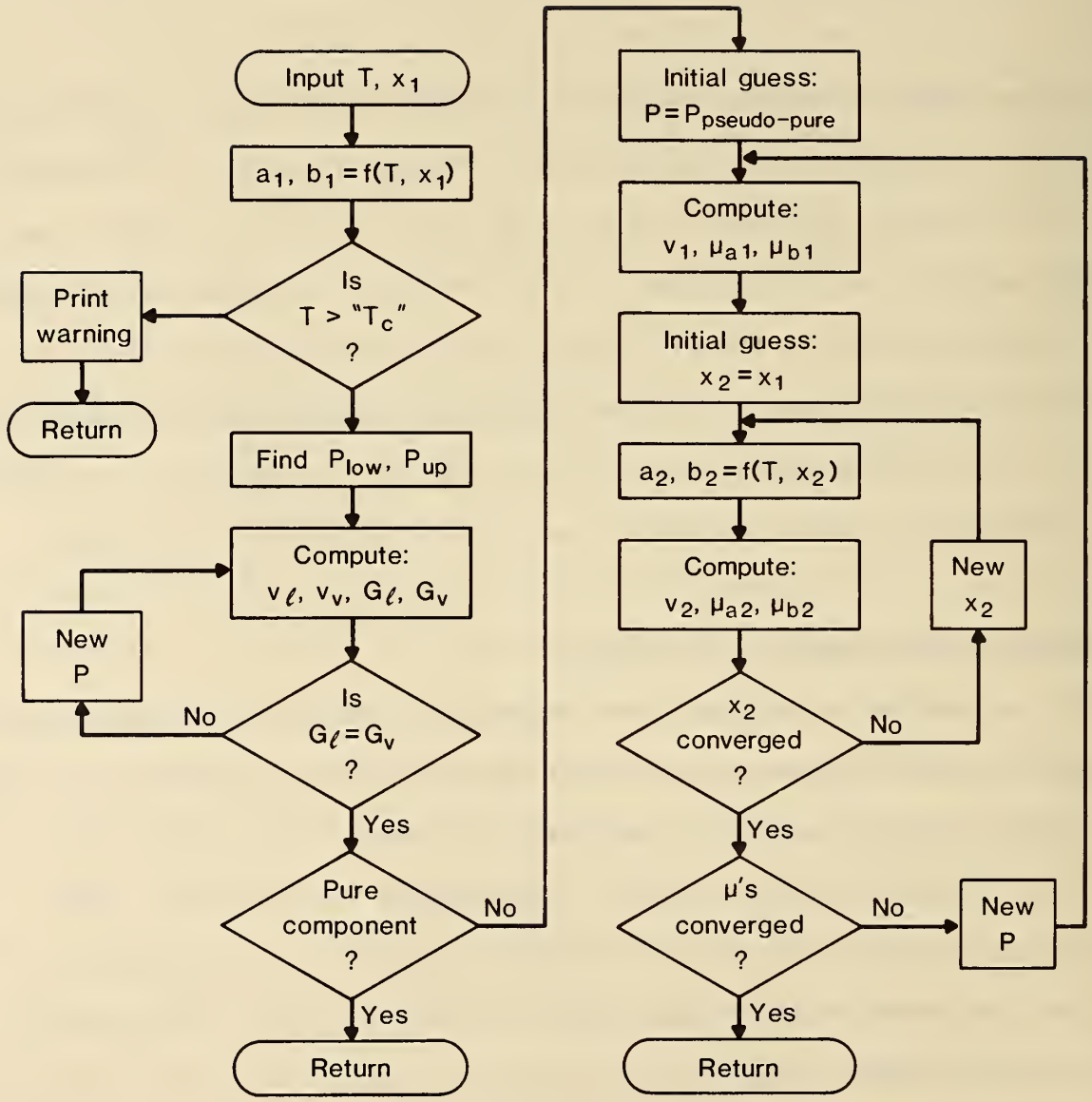

Figure 6.2. Flow chart for the calculation of dew or bubble point pressure

Iteration Technique

Several iterative calculations required to compute thermodynamic quantities employ a combination of the secant and reguli-falsi methods to converge to a solution. The equations to be solved are arranged to give a function $\Psi(\theta)$ which is zero at the converged value of the iteration variable, θ. In the secant method an improved guess for θ is generated by assuming a linear function $\Psi(\theta)$ between two successive guesses and solving for $\Psi(\theta) = 0$:

$$\theta^{(i+1)} = \theta^{(i)} - \Psi(\theta^{(i)}) \frac{\theta^{(i)} - \theta^{(i-1)}}{\Psi(\theta^{(i)}) - \Psi(\theta^{(i-1)})} \tag{6.29}$$

where the superscript is the iteration index. This is represented in Figure 6.3 as the extrapolation from points (2) and (3) to find $\theta^{(4)}$. (If the derivative $\partial\Psi/\partial\theta$ can be expressed analytically the bracketed term in Eqn. 6.29 is replaced by $1/(\partial\Psi/\partial\theta)$ to generate Newton's method.) The most recent values of θ and $\Psi(\theta)$ are retained and the iteration continues. The reguli-falsi method is similar except that the new guess for θ is based on points having a positive and negative value of Ψ:

$$\theta^{(i+1)} = \theta^{(pos)} - \Psi(\theta^{(pos)}) \frac{\theta^{(pos)} - \theta^{(neg)}}{\Psi(\theta^{(pos)}) - \Psi(\theta^{(neg)})} \tag{6.30}$$

This method is shown in Figure 6.3 as the interpolation between points (1) and (3); note that the oldest guess for θ is not necessarily discarded.

Given starting values for θ which result in positive and negative values of $\Psi(\theta)$ (such as the pressure iteration starting at p_{low} and p_{up}) the reguli-falsi method bounds the solution and will always converge for a continuous function $\Psi(\theta)$.

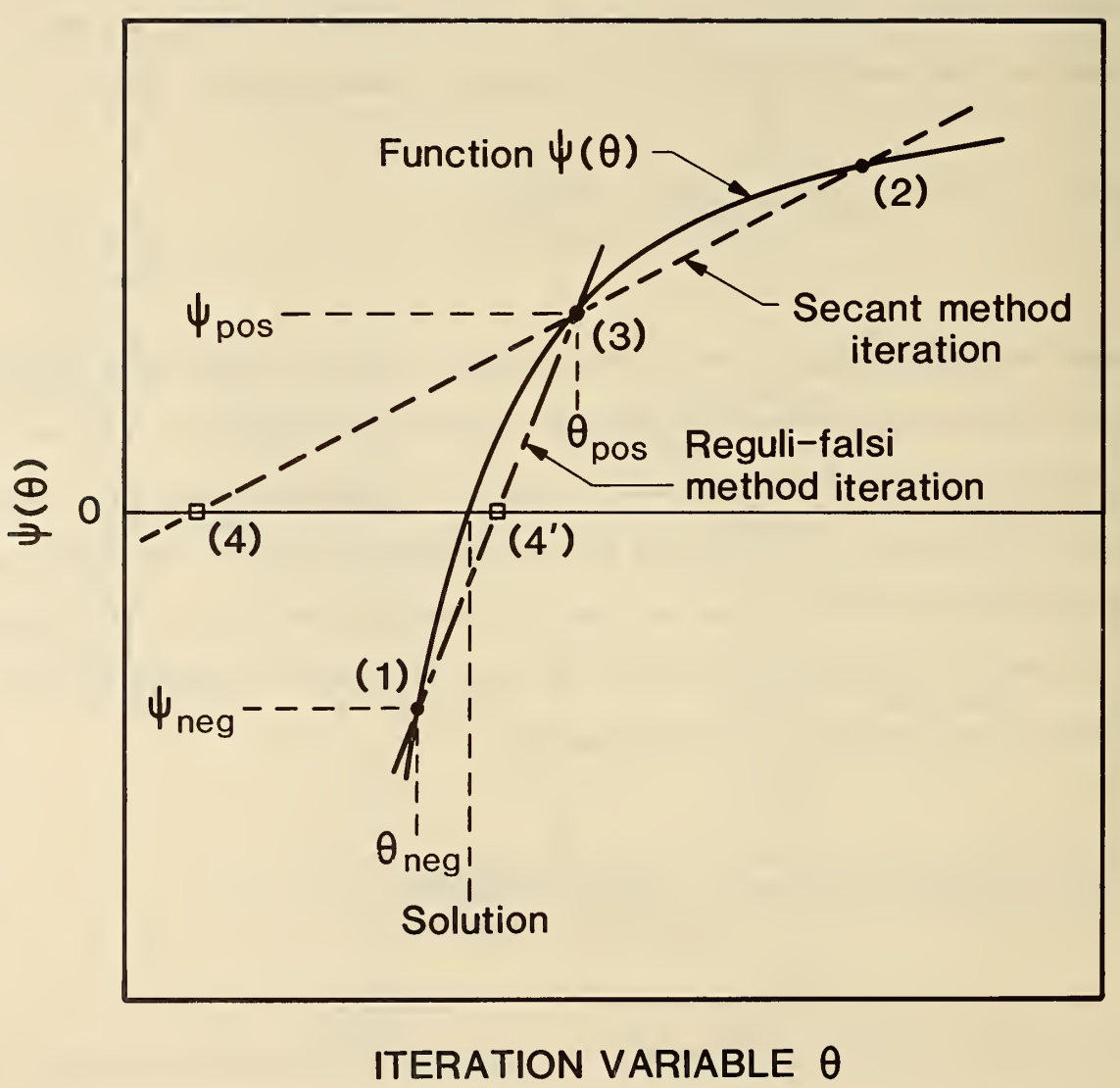

Figure 6.3. Graphical representation of the secant and reguli-falsi iterations to solve for $\psi(\theta) = 0$.

The secant method, because it is always based on the two most recent guesses of θ, often converges faster but can also fail to converge or even diverge from the solution. In combining these two methods, a new guess for θ is generated by the secant method. However, the information necessary for the reguli-falsi method is retained so that if $\theta^{(i+1)}$ given by the secant method lies outside the bounds set by reguli-falsi (i.e., $\theta^{(pos)}$ and $\theta^{(neg)}$) a new guess for $\theta^{(i+1)}$ is generated. For example in Figure 6.3, the secant method extrapolation from (2) and (3) to $\theta^{(4)}$ is diverging from the solution in this case the reguli-falsi interpolation between (1) and (3) is used to compute a new guess, $\theta^{(4')}$.

7. EXAMPLES OF THE APPLICATION OF THE CSD EQUATION OF STATE

In this section, the perturbed hard-sphere equation of state developed in the preceeding sections is applied to a particular class of fluids--the halogenated hydrocarbon refrigerants--and their mixtures. First, the thermodynamic characteristics of 11 pure refrigerants as represented by the equation of state are compared with published values. For most of these fluids, tabular values taken from ASHRAE (1981) are used, however, a detailed discussion for R113 using the original literature data is also included. Finally, the ability of the equation of state to represent the behavior of mixtures is considered for two cases: the nonazeotropic mixture R13B1/R152a and the system R22/R12 which has an azeotrope.

Pure Refrigerants

The saturation data of ASHRAE (1981)* were used to generate the a and b parameters of the equation of state for 11 common one- and two-carbon halogenated hydrocarbon refrigerants. The saturation pressure and saturated liquid and vapor volumes over a reduced temperature range of approximately 0.6 to 0.9 were supplied (with equal weighting) to the programs described in Section 6 to obtain the a and b which best fit the data at a particular temperature. These individual values were then fit to the following functions of temperature:

$$a = a_0 \exp(a_1 T + a_2 T^2) \tag{7.1}$$

$$b = b_0 + b_1 T + b_2 T^2 \tag{7.2}$$

*The data of the 'SI Unit Formulations' were used; these data are improved and revised from earlier ASHRAE compilations presented in English Units.

These temperature dependancies are equivalent to those suggested by DeSantis, et al. (1976) except for the addition of the T^2 terms. The perfect gas heat capacities, C_p^o, were obtained from literature values derived from spectroscopic measurements and were fit over a limited temperature range to the function:

$$C_p^o = c_0 + c_1 T + c_2 T^2 \tag{7.3}$$

The values of the a_i, b_i and c_i for each refrigerant are given in Appendix A.

The success of the equation of state in representing the ASHRAE data is indicated in Table 7.1. The differences between the tabulated values and those predicted by the equation of state (using the a and b given by Eqn. 7.1 and 7.2) are listed as RMS differences over the temperature range indicated. The RMS differences for the saturation pressure ranged from 0.10 to 1.34 percent with an average for all 11 refrigerants of 0.54 percent. The liquid volume representations ranged from 0.01 percent to 0.34 percent with an average of 0.09 percent. The RMS error for the vapor volume ranged from 0.14 to 1.16 percent with an average of 0.50 percent. These differences are on the same order as the accuracy to which the corresponding experimental quantities are known (for example, see Mears et al. (1955)).

The temperature dependence of the differences in saturation pressures and volumes for R12 and R22 are shown in figures 7.1 and 7.2. The smooth curves are a result of comparing the equation of state with tabular data generated by another correlation rather than with experimental measurements. The greater differences at higher temperatures are primarily a result of the approaching

Table 7-1. Comparison of ASHRAE and Equation of State Values of Saturation Pressure, Saturated Liquid and Vapor Volume, and Enthalpy of Vaporization for 11 Pure Refrigerants

Refrigerant	Temp. Range of Correlation (K)	RMS Difference (%)*			
		p_{sat}	V_ℓ	V_v	ΔH_{vap}
R11	240-420	0.41	0.04	0.45	0.87
R12	200-340	0.26	0.05	0.29	0.74
R13	180-272	0.10	0.02	0.14	0.17
R13B1	200-300	0.64	0.07	0.57	1.46
R14	140-200	0.18	0.01	0.18	0.35
R22	220-330	0.50	0.06	0.45	1.13
R23	180-272	1.34	0.17	1.16	2.88
R113	240-430	0.22	0.03	0.23	0.61
R114	210-370	0.72	0.34	0.70	2.33
R142b	220-360	0.92	0.10	0.83	2.41
R152a	200-340	0.62	0.09	0.53	1.88
Average		0.54	0.09	0.50	1.35

$$*\text{RMS Difference} = \frac{1}{N}\left[\sum_{i=1}^{N}\left(\frac{\text{ASHRAE} - \text{EOS}}{\text{EOS}} \times 100\%\right)^2\right]^{1/2}$$

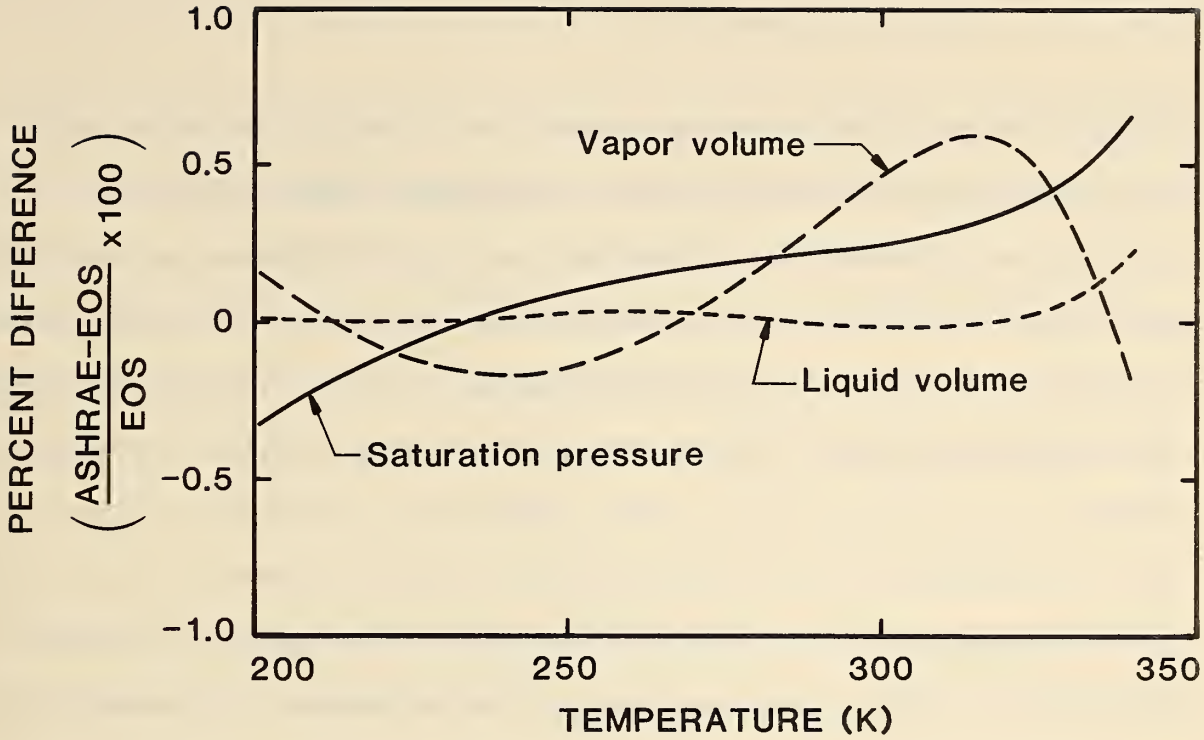

Figure 7.1 Percent difference between ASHRAE values of saturation pressure and liquid and vapor volumes for R12 and values correlated by equation of state.

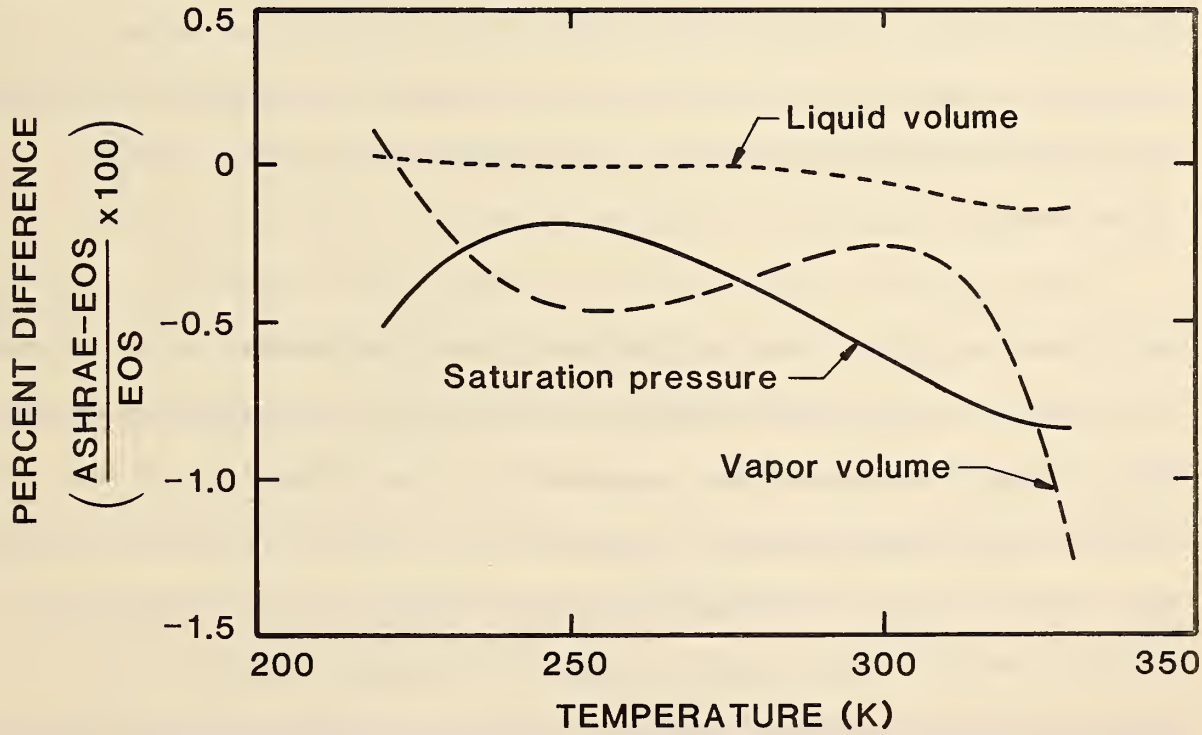

Figure 7.2 Percent difference between ASHRAE values of saturation pressure and liquid and vapor volumes for R22 and values correlated by equation of state.

critical point; there is also an increased error in Eqn. 7.1 and 7.2 in representing a and b at the extremes of temperature used in the data correlations. The equation of state consistently overpredicts the pressure and volumes for R22 (fig. 7.2). Although one might expect the differences to be centered about zero, the observed behavior is the result of simultaneously fitting three quantities with two parameters which interact in the equation of state.

A more stringent test for the equation of state is its ability to predict quantities not used in the correlation of the parameters. The enthalpy of vaporization is such a quantity (and one that is independent of C_p^o). The RMS differences between the predicted and tabulated values (given in Table 7.1) vary between 0.17 and 2.88 percent with an average of 1.35 percent. Although these differences are larger than those for the pressure and volumes it is important to note that in many cases the enthalpy values reported in ASHRAE are not measured calorimetrically but are derived from p-V-T and C_p^o information.

The estimation of heat capacity involves a second derivative of the equation of state and is thus a particularly stringent test of physical consistency. The equation of state has been integrated over the volume to give the Helmholtz free energy function, from which all the other functions, including heat capacity, arise. Associated with that integration is a temperature-dependent constant which can be evaluated by knowning the perfect gas heat capacity of the fluid(s) of interest. As a test of the equation of state let us compare values of C_p for the saturated liquid state of R152a from several sources. The values calcualted by the equation of state use the perfect gas

properties presented by Chen et al. (1975). Also considered are the values of C_p appearing in the ASHRAE (1981) tables, an experimentally-based data correlation published by the National Engineering Laboratory (Cartwright, 1981) in the United Kingdom, and a single experimental value of C_p measured by Radermacher (1983). These four sets of information are compared in figure 7.3. The four sets agree well at the high-temperature end of the range. At lower temperatures, however, the ASHRAE values are consistently below the experimental information of NEL and Radermacher; this is an indication of the shortcomings of data correlation schemes that are in common use. The most striking feature of figure 7.3 is that the values of C_p predicted by the equation of state compare well with experimental information even though they have been evaluated without reference to any previously measured liquid heat capacities.

Because of the data smoothing and correlation necessary to generate complete sets of properties such as the ASHRAE tables, the use of original literature data to generate the equation of state coefficients would have been preferable. The ASHRAE tables, while not always based on the most recent refrigerant data, represent an extensive compilation in a uniform format and were thus a convenient source for the correlation of coefficients. The formulation for 1,1,2-trifluorotrichloroethane (R113) given in ASHRAE is that of Mastroianni, et al. (1978). The consequences of basing the equation of state correlation on tabular data will be examined for this fluid.

Mastroianni, et al. report the saturation pressure of 0.9999^+ pure R113 at 26 temperatures with an estimated accuracy of 0.1 percent for pressure and 0.02 to 0.05 °F (0.01 to 0.03K) for the temperature of the thermostated bath,

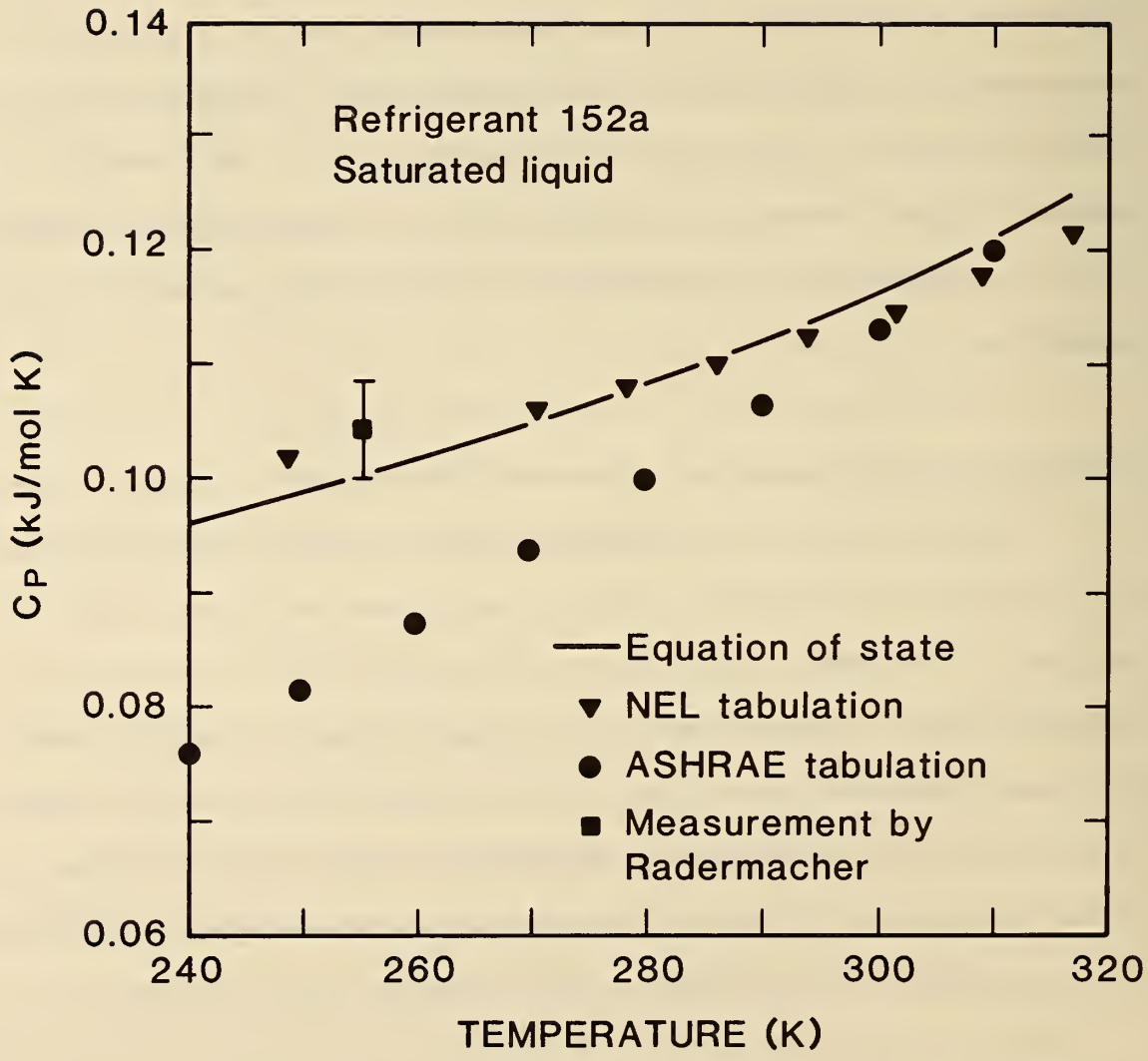

Figure 7.3 A comparison of the molar heat capacity at constant pressure for saturated liquid R152a given by several sources

saturated liquid density at 9 temperatures with an accuracy of 0.1 percent; and the p-V-T behavior of superheated vapor along 7 isochors at 0.1 to 1.2 times the critical density (yielding 42 data points) with a volume uncertainty of 0.01 percent and temperature and pressure uncertainties as stated above. They also measured the critical temperature but obtained the critical pressure and volume by extrapolation. Using these measurements they fit the saturation pressure to a 6 parameter expression for $\ell n\ (p_{sat})$ as a function of T to obtain an RMS error of 0.28 percent. The 9 liquid density measurements were represented by a 5 parameter expression with an RMS error of 0.12 percent. The p-V-T behavior of the superheated vapor was represented with an RMS error of 0.20 percent using the Martin-Hou equation of state (involving 13 parameters plus the critical temperature). These correlations were combined with a 5 parameter expression for the perfect gas heat capacity to generate a complete set of thermodynamic tables and a pressure-enthalpy chart (which are reproduced in ASHRAE).

We now compare the literature data with the values predicted by the hard sphere equation of state using a and b parameters based on ASHRAE data. The agreement for the saturation pressure and saturated liquid volume (quantities which were used in the correlation of a and b) shown in figure 7.4 are excellent for reduced temperatures below 0.9 (439 K). The RMS error over the temperature range of the correlation (240-430 K) is 0.038 percent for liquid volumes and 0.29 percent for saturation pressures. These deviations are only slightly greater than those given in Table 7.1; they are also nearly identical to those of Mastroianni, et al. over the same temperature range. Thus the use of tabular data for R113 does not appear to degrade the fit of the equation of state for conditions which are within the limits of both the correlation which

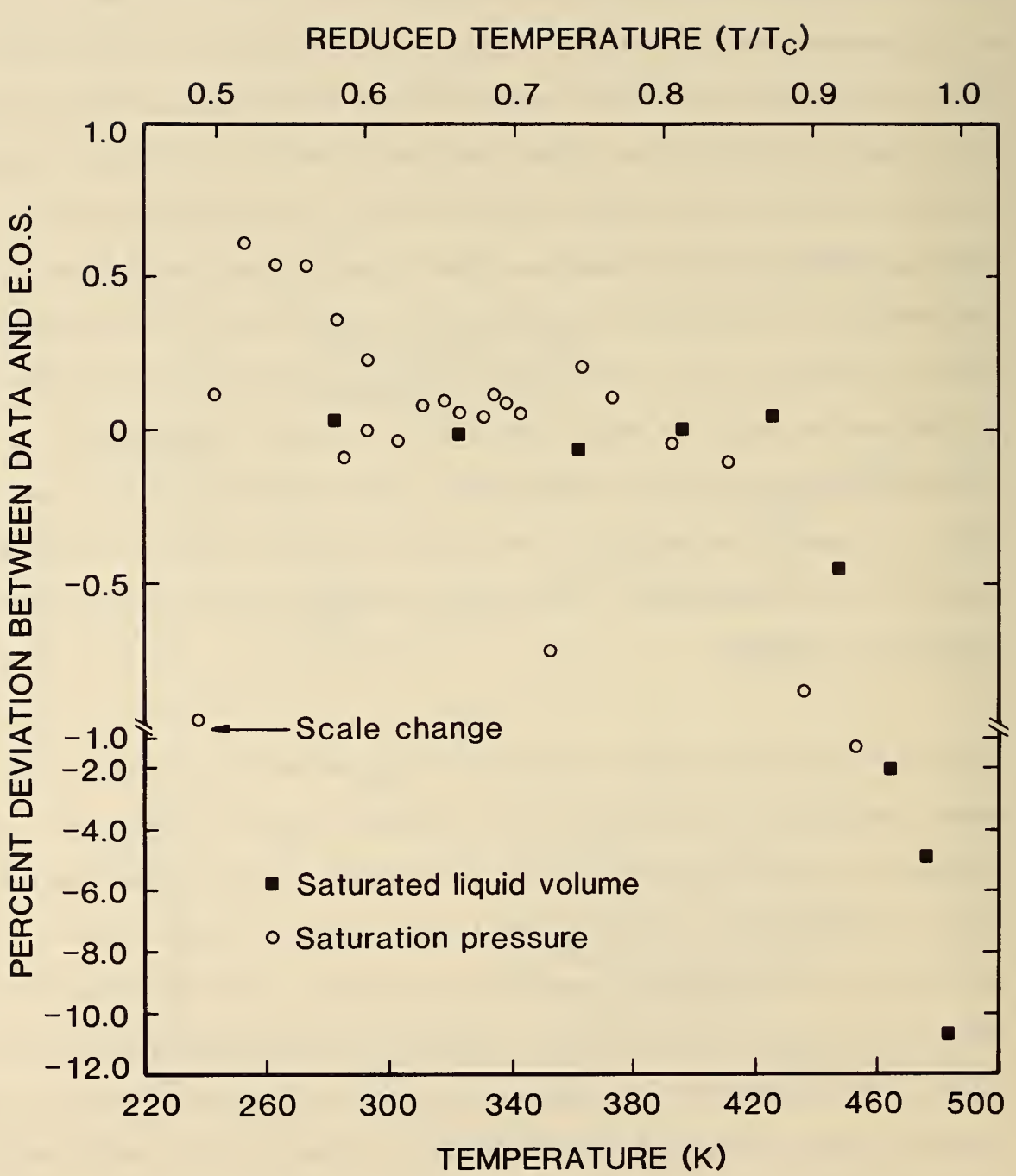

Figure 7.4 Percent difference between values of saturation pressure and saturated liquid volume correlated by equation of state and experimental data of Mastroianni et al. (1978) for R113.

generated the tabular data and the correlation of the CSD equation of state parameters.

The equation of state parameters were generated using saturation data from 240 to 430 K. As shown in figure 7.4 the predicted saturation pressure and liquid volume show serious deviations (as great as 10 percent) outside these bounds. This behavior is an indication of the inability of the CSD equation of state to quantitatively reproduce the critical region rather than a consequence of merely extrapolating beyond the limits of the correlation.

A comparison of experimental and predicted pressures as functions of temperature and volume in the superheated vapor range is shown in figure 7.5. Apart from the critical region, the equation of state exhibits commendable accuracy upon extrapolation to higher temperatures and/or away from saturation. Note that the behavior at the critical temperature is accurately represented as long as the actual critical region is avoided. Even though the parameters were fit using only saturation data below 430K the equation of state predicts the pressure of superheated vapor to within 1.2 percent at temperatures as high as 532 K for reduced volumes between 1.43 and 10.0. The hard sphere equation of state represents the behavior of fluids in a physically meaningful way and thus, with care, it can be extrapolated within reasonable bounds in the absence of data.

The correlation discussed up to this point was based on the saturation data of ASHRAE. We now discuss a correlation of the equation of state based directly on the data of Mastroianni, et al. This data was used with a non-linear least squares technique as discussed in Section 6 to simultaneously generate the

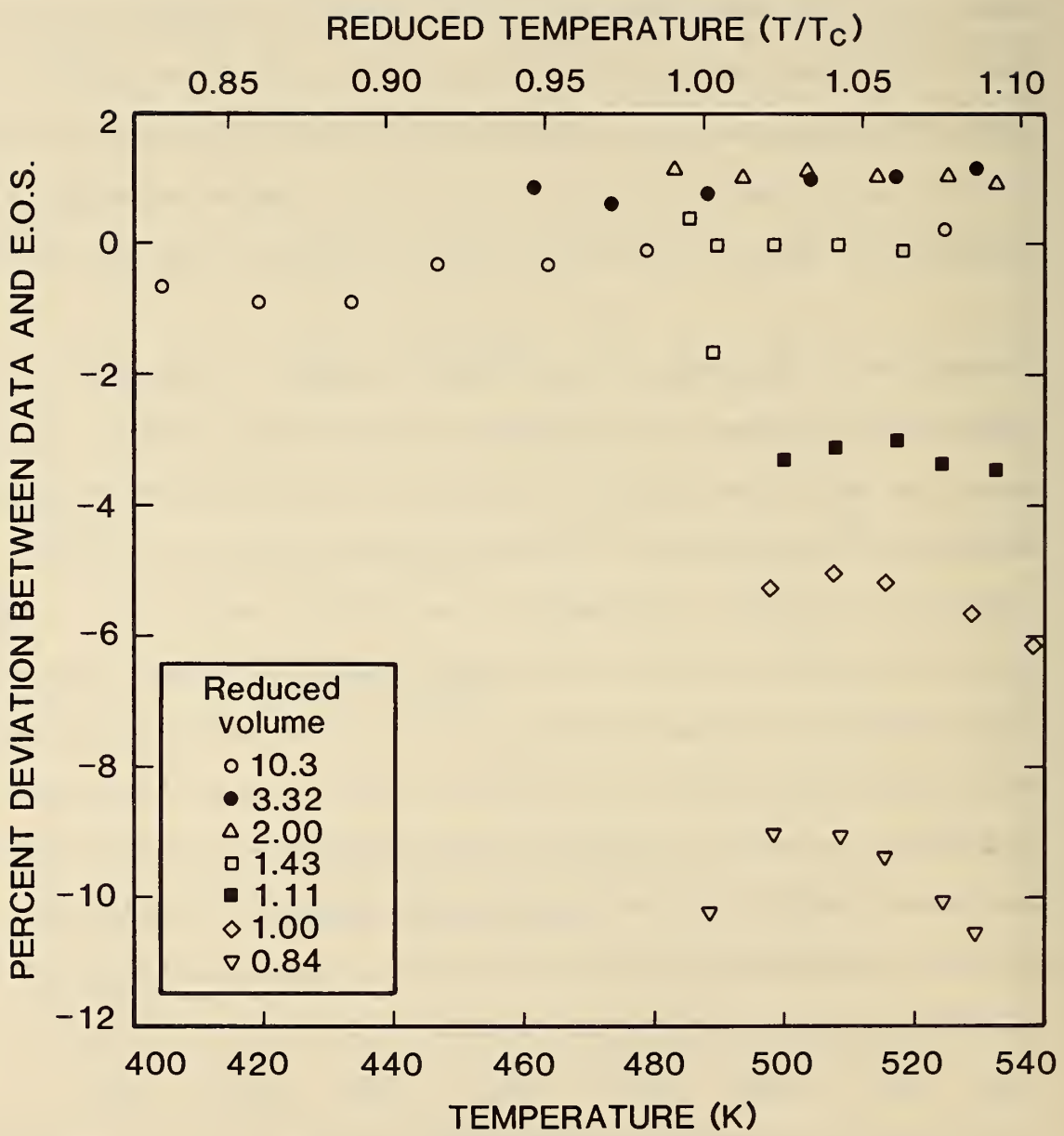

Figure 7.5 Percent difference between values of pressure in the superheated vapor region as a function of temperature and reduced volume (V/V_c) correlated by the equation of state and experimental data of Mastroianni, et al. (1978) for R113.

coefficients a_0, a_1, a_2, b_0, b_1, b_2 (the ASHRAE-based values were used as the initial estimates to start the iteration). Saturation data at reduced temperatures above 0.9 were excluded from the correlation as were superheated vapor data with reduced volumes below 1.5. The saturated liquid volumes were given a greater weight than the pressure data to reflect the greater accuracy of this measurement and also to give approximately equal total weights to each of the three data types. As indicated in Table 7.2, the individual a_i and b_i changed by as much as 31 percent between the two correlations. The values of the actual a and b parameters, however, changed only slightly as indicated in Table 7.2 for two representative temperatures. With the correlation based on the literature data the fit of the superheated vapor is improved at the expense of a slightly degraded fit for the saturation data. The total sum of squares of the residuals decreased by 15 percent for the correlation based on the literature data.

This comparison of the CSD equation of state with the original literature data for R113 demonstrates the power of this expression to represent the p-V-T behavior of a pure fluid. With the exception of the critical region, it represents saturated liquid volumes to better than 0.1 percent and saturation pressures and the pressures of superheated vapor on the order of one-half of one percent. More importantly the CSD equation of state achieves these accuracies for both liquid and vapor with a single expression involving only six adjustable parameters plus the three coefficients needed to represent C_p^o. This is in contrast to the three separate expressions for R113 presented by Mastroianni et al. involving a total of 25 parameters.

Table 7.2 Comparison of Data Correlations for R113 Based on Saturation Data of ASHRAE and Saturation Plus Superheated Vapor Data of Mastroianni et al.

	Correlation Based on Data of:	
Equation of State Parameters	ASHRAE	Mastroianni
a_o (kJ $m^3/kmol^2$)	7332.59	7489.98
a_1 (kJ $m^3/kmol^2$ K)	-2.20396×10^{-3}	-2.34255×10^{-3}
a_2 (kJ $m^3/kmol^2$ K^2)	-7.26560×10^{-7}	-5.03625×10^{-7}
b_0 (m^3/kmol)	0.230713	0.233100
b_1 (m^3/kmol K)	-1.87956×10^{-4}	-2.03232×10^{-4}
b_2 (m^3/kmol K^2)	-1.06114×10^{-7}	-0.82063×10^{-7}
a @ T = 300 K (kJ $m^3/kmol^2$)	3545.8	3544.8
a @ T = 400 K (kJ $m^3/kmol^2$)	2703.4	2707.3
b @ T = 300 K (m^3/kmol)	0.16478	0.16474
b @ T = 400 K (m^3/kmol)	0.13855	0.13868
RMS deviation between EOS Prediction and Data of Mastroianni (%)		
$V_{liq,sat}$ (T = 282 - 425 K, 5 points)	0.038	0.057
P_{sat} (T = 238 - 436 K, 23 points)	0.38	0.51
P_{vap} (T = 405 - 532 K, V_r = 2.0 - 10.0, 19 points)	0.85	0.59
Sum of squares of residuals:	16.61	14.19

Equilibrium Properties of the Mixture R13B1/R152a

As an example of a mixture which does not have an azeotrope we examine the R13B1/R152a system. There is little published information about this mixture and thus measurements of the saturation properties were undertaken at NBS. The experimental details and measurements are presented elsewhere (Morrison and Neal, 1985) but are briefly described here before proceeding to a discussion of the correlation of the data with the equation of state.

Samples for this study were prepared by distilling measured quantities of each of the components from a gas buret into a stainless steel thermocompressor at liquid nitrogen temperature. The amount of each of the components was determined in two ways: first by using the temperature-pressure-volume measurements from the gas buret and the values of the second virial coefficient predicted by the equation of state described earlier in this paper (Eqn. 2.2); second, by weighing the thermocompressor after each successive addition of the components (Morrison and Kincaid, 1983). The second virial coefficient for R152a agreed within experimental uncertainty with the values listed by Dymond and Smith (1969); those values were derived from the measurements of Mears et al. (1955). Second virial coefficients for R13B1 were not available in the literature. The two amount determinations typically agreed with one another to 0.1%. The measurements included runs on each of the pure refrigerant materials and on mixtures that were roughly 25, 33, 50, 67, and 75 mole percent R152a. The mixtures were moved from the thermocompressor into the sample cell, constructed from a drawn sapphire tube having a volume of approximately 7.0 cm^3 (Davis, 1983). The volume accessible to the sample could be changed by raising and lowering the mercury level in the sapphire tube.

The cell was kept in a water bath whose temperature was measured with a quartz crystal thermometer calibrated to an accuracy of 0.001 K with an NBS-calibrated 25 ohm platinum resistance thermometer, the temperature was controlled to within 0.0003 K of a constant value. The total volume accessible to the sample and the volumes of the individual phases were determine by measuring the distances between the top of the cell and the liquid-vapor meniscus or the liquid mercury meniscus. The volume of the cell was calibrated to within 0.001 cm^3 with triply distilled mercury. Pressures were measured with a differential gauge calibrated to 0.2 kPa with a dead weight gauge.

Measurements of the liquid and vapor volumes and the pressure were made at five equally spaced temperatures between 15°C and 55°C. Several sets of measurements were made by progressively enlarging the volume accessible to the sample. The results most immediately determined from these data are the liquid molar volume and the pressure on the bubble line. Although no samples of either phase were taken during the experiments, there is sufficient information in these data to locate the dew point curve (Knobler and Scott, 1982).

The bubble point pressures are shown as open circles in figure 7.6. The filled circles represent the composition of the dew phase in equilibrium with the 50% mixture calculated from the data. The molar volumes of the saturated liquid are shown in figure 7.7.

The equation of state was generated by first fitting the properties of the pure materials in the fashion refered to in Section 6. A value of 0.089 for the mixing parameter was found to optimize the pressure correlation along

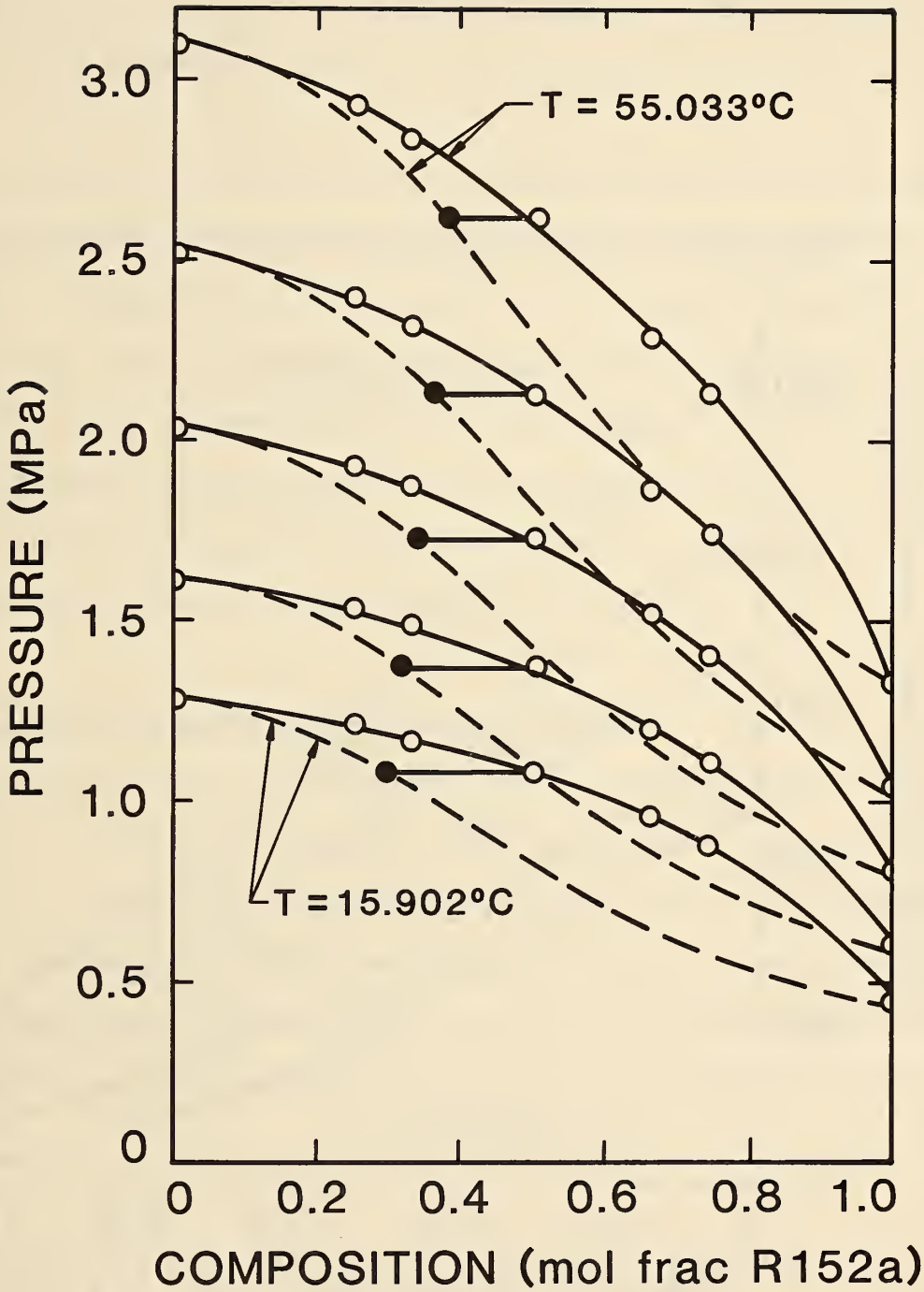

Figure 7.6 Saturation pressure for the mixture R13B1/R152a. The open circles, O, are experimental bubble points and the closed circles, ●, dewpoints. The solid and dashed curves are the predicted bubble and dew curves respectively beginning at the lowest pressure and temperature, 15.902°C and incresing in temperature to 25.323°C, 35.323°C, 45.134°C, and 55.033°C.

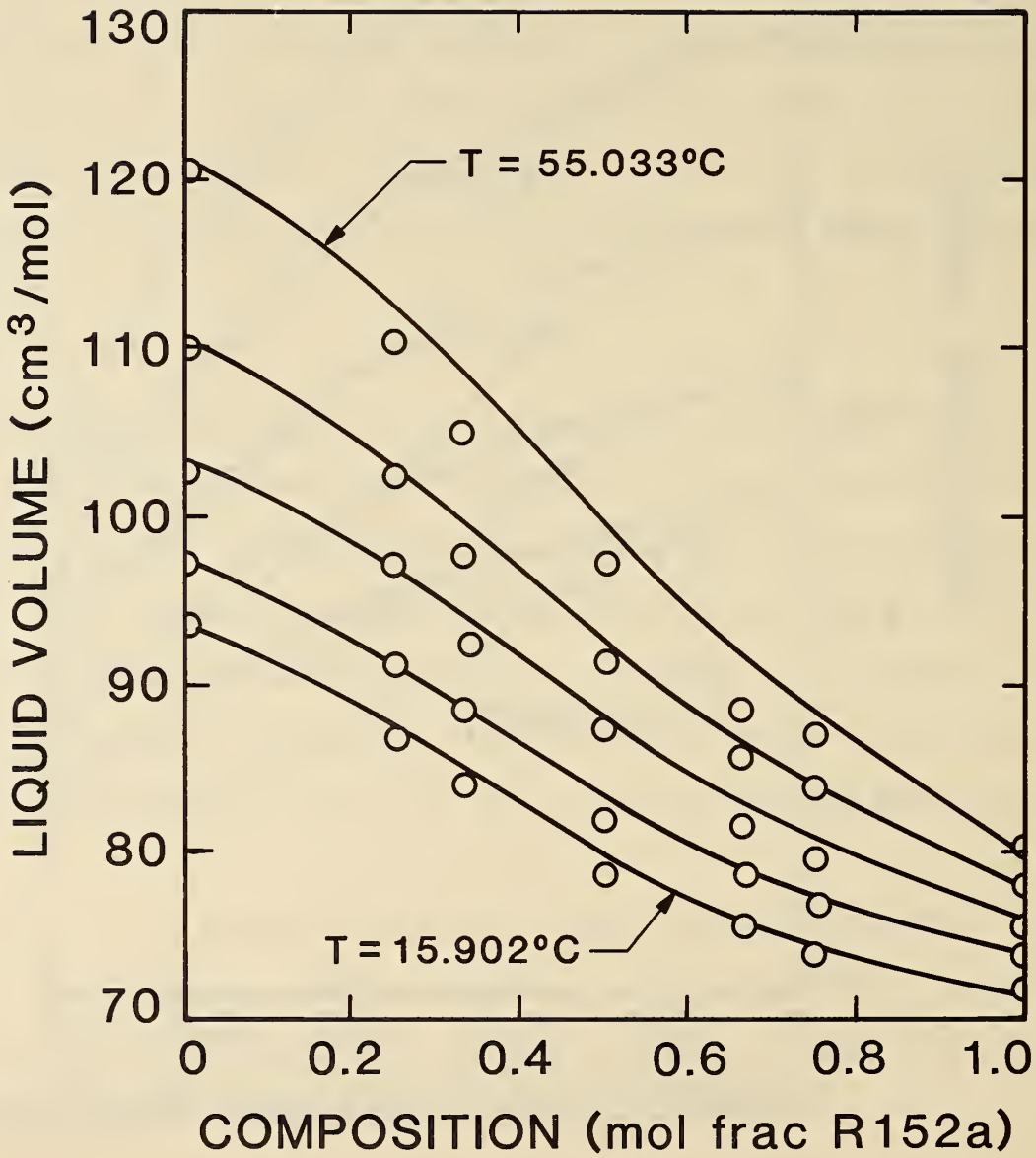

Figure 7.7 Saturated liquid volumes for the mixture R13B1/R152a. The open circles are the measured values and the lines, the values predicted by the equation of state. The temperatures are identical to those of Figure 7.6.

the bubble curve. We elected to use only the pressure data and not include the volume data to find the mixing parameter because of the higher precision of the pressure measurement.

The pressures and liquid volumes given by the equation of state are shown in figures 7.6 and 7.7 as solid and dotted curves for the bubble and dew lines respectively. The pressures are correlated to +/- 5 kPa; the predicted volumes for the mixture are consistently greater than the measured volumes. One should note the dramatic narrowing of the two phase region on the R13B1 side of the phase diagram, especially at the highest temperature. This behavior does not indicate the onset of an azeotrope, rather it is an indication of the nearness of the R13B1 critical point at 67°C.

Azeotropes and the Equilibrium Properties of R12/R22

In the above discussion, we examined the simplest kind of behavior one can expect from a mixture of two liquids, complete miscibility and the monotone variation of properties from one component to the other. We now consider an example of the next most complex behavior case, azeotropy. Our motivation is twofold, first, to discuss the situations when one can expect an azeotrope, and second, to examine a refrigerant mixture for which there is calorimetric data.

Let us consider the situation when one would expect an azeotrope. An azeotrope is inevitable when the saturation curves of the two components cross the p-T projection. Such a point of apparent intersection is called a 'Bancroft point' (Rowlinson and Swinton, 1982b). The mixture R12/R152a, also known as R500, shows just such a behavior. In mixtures where there is a

Bancroft point, the azeotrope can exist over the entire composition range from one pure component to the other. In R12/R152a the locus of azeotropes is intercepted by the solid phase and the critical locus (Pennington, 1952). A Bancroft point is not required for an azeotrope to exist. Since any kind of non-ideal behavior causes a deviation from the Raoult law prediction, the closer the vapor pressures of the two components, the more likely there will be an extremum in the T-x or p-x lines and, hence, an azeotrope. Closeness of vapor pressures is often associated with closeness of critical temperatures, since, with a few notable exceptions, the critical pressure of many materials (including halogenated hydrocarbons) are nearly the same, about 4 MPa, and saturation lines are roughly parallel in a p-T projection. One can thus conclude that two materials with nearly the same critical temperature are likely to show azeotropic behavior. A sharp demarcation cannot be drawn, however. A certain critical temperature difference needn't guarantee the presence or absence of an azeotrope; the situation depends upon the detailed molecular character of the components in the mixture.

The mixture R12/R22, also known as R501, has an azeotrope that emerges from the pure R22 axis of the phase diagram at approximately 320 K and moves into the mixture region as the temperature is lowered until, at 253 K, the azeotropic composition is approximately 10 mol percent R12 (Spauschus, 1962). The variation of the azeotropic composition with temperature is not unusual. The amount by which it varies with the temperature will however, be different from one azeotropic mixture system to another. The azeotrope in R12/R22 is a positive azeotrope (Rowlinson and Swinton, 1983b); that is, the boiling curve will have a maximum pressure when measured at constant temperature or, conversely, a minimum temperature when measured at constant pressure. This is

the kind of azeotrope one would typically expect from refrigerant mixtures. The opposite kind of behavior is usually encountered when the two components have a strong attractive interaction, such as the hydrogen bonding encountered in chloroform/acetone (Karr et al., 1951).

The mixture R12/R22 shows azeotropic behavior over a range of temperatures and compositions as shown in fig. 7.8. The azeotropic point is typically found by locating an extremum in the bubble point curve; at such a extremum, the second law of thermodynamics requires the liquid and vapor phases to have the same composition and the dew and bubble lines to be tangent (Bett et al., 1975). Because of the flatness of these lines around an azeotrope, the uncertainty in the composition is typically large. The data of Eiseman (1957), for example determine the azeotrope only to within 5 mole percent as shown by the error bar in figure 7.8. The azeotropic composition can be determined more accurately by a distillation process (Pennington, 1952).

The equation of state parameters for pure R12 and R22 were determined by using data from the ASHRAE Tables (1981) as described above. The mixing parameter was determined by fitting the bubble point predicted by the equation of state to the constant pressure boiling temperatures measured by Eiseman (1957) over the full range of compositions. The values of the mixing parameter were slightly composition dependent. Equally weighting all values over the entire composition range yielded an average of 0.041 with a standard deviation of 0.009.

The first test of the equation of state is the comparison of its prediction of the temperature dependence of the azeotropic composition. The solid curve in

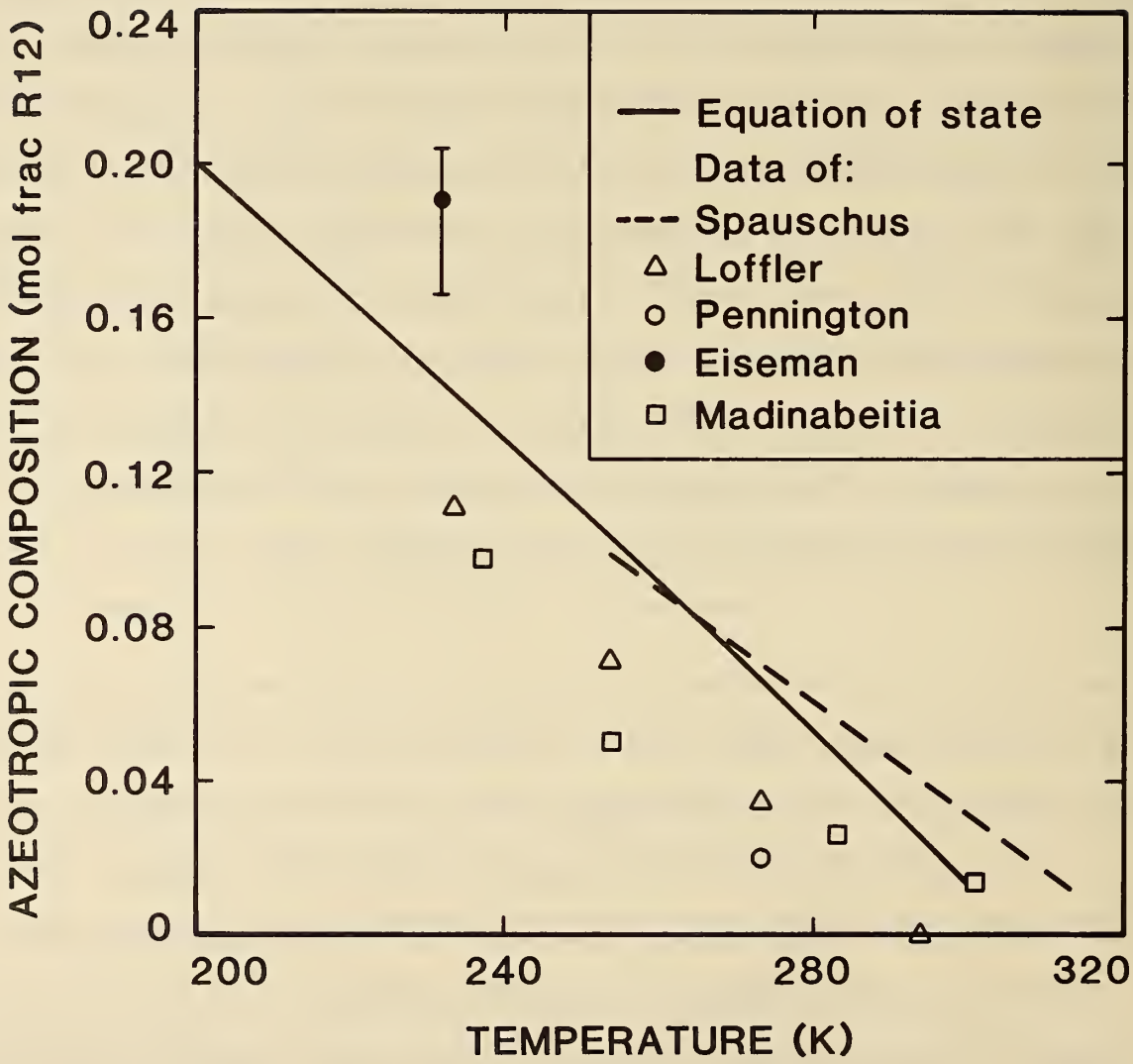

Figure 7.8 The variations of the azeotropic composition of the R12/R22 mixture as reported by several authors and predicted by the equation of state.

figure 7.8 shows that this prediction falls within the experimental measurements of the azeotrope. As we have noted previously, there is considerable uncertainty in those points. The dashed line in the figure is the locus suggested by Spaschus (1962) from measurements he made on a grid of composition-temperature conditions. Our prediction, which arises from data at a single pressure nearly coincides with Spauschus's experimental locus.

The equation of state contains enough information to evaluate enthalpies as long as the temperature is fixed. (For differences in enthalpy due to temperature changes, one also needs the perfect gas heat capacities.) Neilson and White (1959) have measured the enthalpy change associated with the complete evaporation of mixtures of R12/R22 over the entire composition range at 222.0 K. Their data, plotted in figure 7.9 are integral quantities because the composition of the liquid changed as the evaporation proceeded. The prediction of a closely related quantity, the enthalpy change associated with the complete vaporization of the liquid mixture at fixed composition to its vapor at the same fixed composition, is shown by the solid curve in figure 7.9. The agreement between these two closely related quantities is on the order of +/- 0.5%. The equation of state also predicts nearly quantitatively the curvature associated with the composition. By using these evaporation data, Neilson and White were also able to evaluate a quantity closely related to the enthalpy of mixing along the saturation line, H^e. The comparison of their calculated values and the predicted values are shown in figure 7.10. The equation of state overpredicts this quantity. One should note however the small magnitude of this quantity. Furthermore, the experimental and equation of state quantities are not exactly the same: the experimental value should underpredict slightly. This comparison with calorimetric data is encouraging.

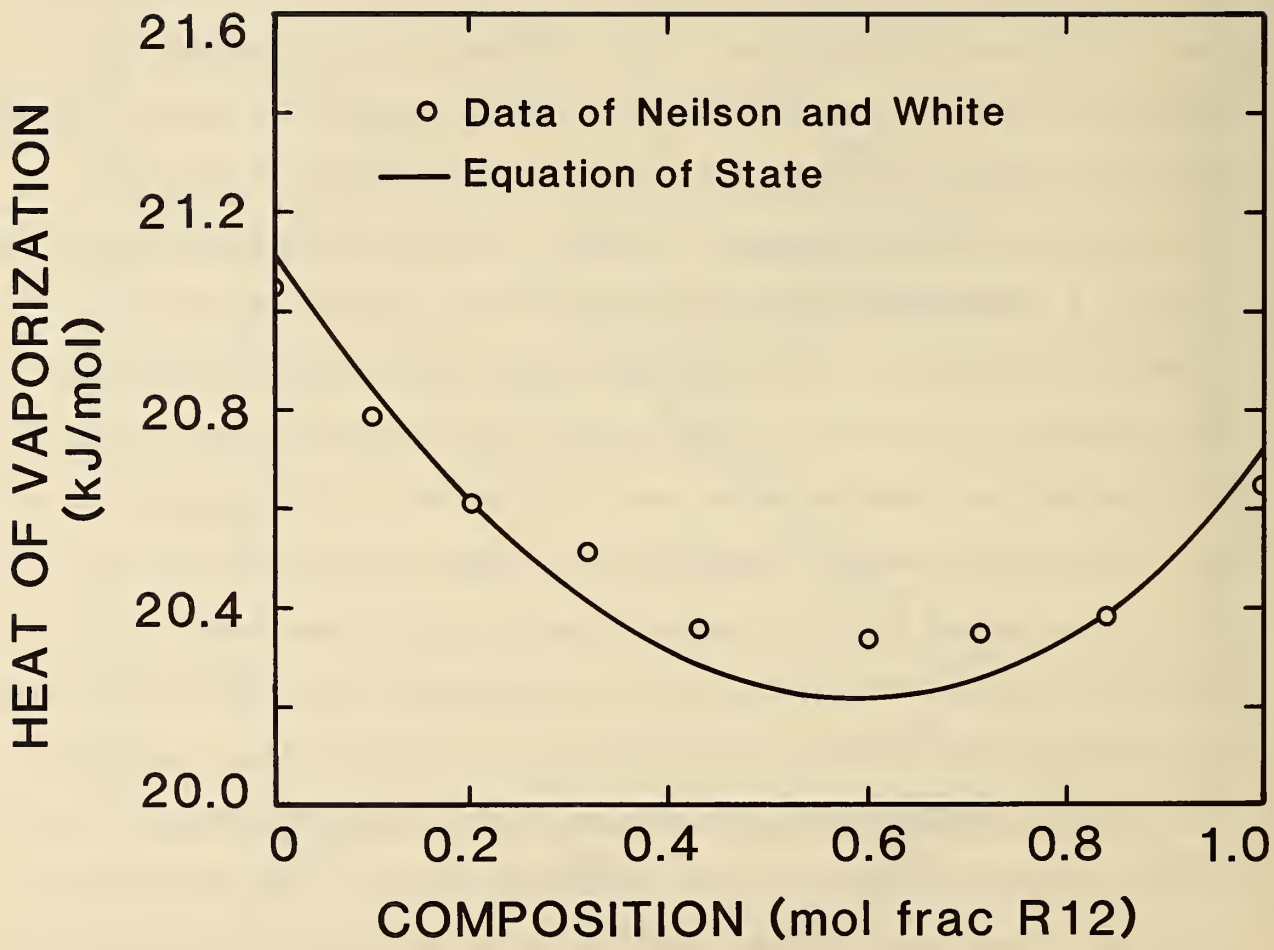

Figure 7.9 The heat of complete vaporization at 222.00K for the mixture R12/R22 as measured by Neilson and White (1959) and predicted by the equation of state.

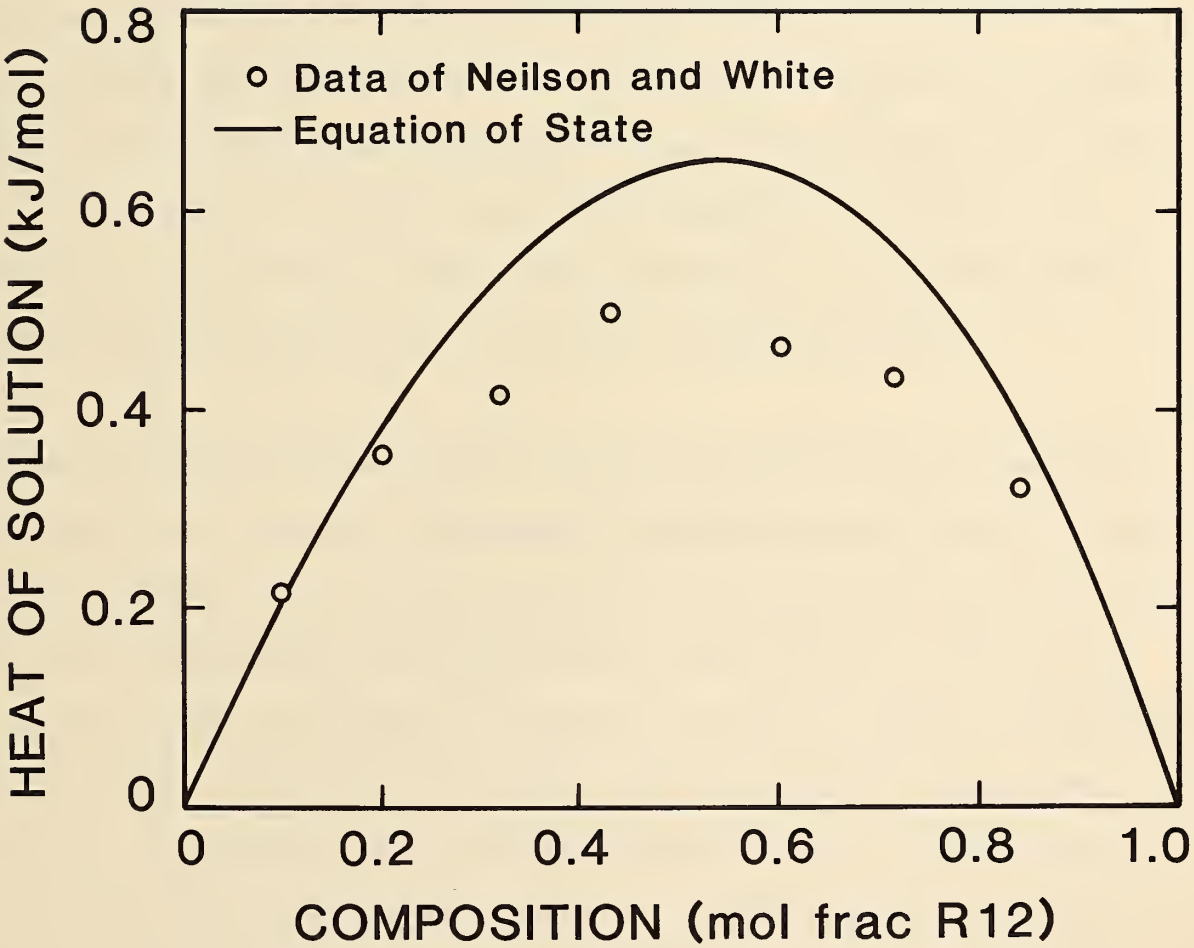

Figure 7.10 The heat of mixing for the R12/R22 mixtures as reported by Neilson and White (1959) and predicted by the equation of state.

That such intricate details about this mixture are accessible through so little information is a demonstration of the power and versatility of the Carnahan-Starling-DeSantis equation of state.

8. CONCLUDING REMARKS

This Note presents the development of an equation of state based on a hard-sphere reference fluid, the expression used is a modification of the Carnahan-Starling-DeSantis (1969) hard-sphere fluid proposed by DeSantis, et al (1976). The resulting expression is simple, based on a good physical model and has a physical interpretation of its parameters. The complete set of thermodynamic functions derived from this equation of state represent with thermodynamic consistency the behavior of both liquid and vapor phases of pure fluids and binary mixtures. The CSD equation of state has been demonstrated to represent the p-V-T properties of the 11 pure refrigerants investigated very well, often within the accuracy to which the experimental quantities are known. It is likely to do equally well for other similar materials (e.g., simple hydrocarbons and hydrocarbon derivatives) and simple inorganic molecules.

The representation of mixture properties with a single interaction parameter (in addition to pure component information) was demonstrated, detailed aspects of mixture behavior were accurately predicted even though the correlation of the interaction parameter was based on limited data. There is, however, a wide range of behaviors possible in mixtures and this is an area that requires continued study. The present mixing rules need to be applied to many more fluid pairs. In addition, the modification of the Carnahan-Starling expression to account for a mixture of hard spheres of differing diameters (discussed in Section 3) should be investigated.

The CSD equation of state concisely represents properties with thermodynamic consistency and permits a rational estimation or extrapolation of quantities

for which no measurements are available. It is not, however, intended to replace experimental data or preclude the need for experimental data covering the entire range of interest.

The representation of both liquid and vapor phases with a single, physically well-founded equation of state is the desirable state of affairs. Therefore, this, or similar, equations of state should be considered as the basis for the preparation of property tabulations for inclusion in handbooks, etc. Such a preparation must be based on a correlation of carefully evaluated experimental data (either original or literature values). Most of the numerical coefficients presented in this work are based on a correlation of tabulated data because of project time limitations and in some cases the unavailability of the original data. For this reason, calculated values based on these coefficients are not meant to replace compilations such as ASHRAE (1981).

At present, the primary use of the equation of state is in studies where the properties of a number of fluids or mixtures are required. A single set of computerized property routines would be usable for different fluids simply by changing the numerical coefficients. Because of the small number of coefficients required, it would be of particular use with fluids for which limited data is available.

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APPENDIX A: EQUATION OF STATE COEFFICIENTS FOR PURE REFRIGERANTS AND MIXTURES

Table A.1. Coefficients for Curve-fits of Pure Component a and b Parameters

Refrigerant	a_o	$10^3 a_1$	$10^6 a_2$	b_o	$10^4 b_1$	$10^8 b_2$	Type of Data	Temp. Range of Data Fit (K)	Source
R11	4971.54	-2.24669	-0.51194	0.176659	-1.74531	-3.49717	p, V_ℓ, V_v @ sat'n	240-420	ASHRAE*
R12	3524.12	-2.77230	-0.67318	0.153755	-1.84195	-5.03644	''	200-340	''
R13	2298.13	-3.41828	-1.52430	0.128141	-1.84474	-10.7951	''	180-272	''
R13B1	2728.10	-2.79791	-1.50848	0.139949	-1.82428	-7.75898	''	200-300	''
R14	1393.60	-4.81985	-1.89167	0.100601	-1.94974	-13.5408	''	140-300	''
R22	2514.59	-2.38706	-1.83653	0.113681	-1.16201	-9.24562	''	200-330	''
R23	2025.93	-4.68206	0.99552	0.103137	-2.29653	15.5760	''	180-272	''
R113	7489.98	-2.34255	-0.50363	0.233100	-2.03232	-8.2063	p_{sat} $V_{\ell,sat}$ $p_v(T,V)$	238-436 282-425 405-532	Mastroianni
R114	9771.35	-5.85557	3.99413	0.306318	-7.96444	78.1059	p, V_ℓ, V_v @ sat'n	210-370	ASHRAE
R142b	2990.00	-0.54056	-4.12642	0.146006	-0.89250	-18.0562	''	220-360	''
R152a	2254.37	-0.58778	-4.37432	0.116521	-0.90488	-11.4563	''	200-340	''

NOTES: $a(\text{kJ m}^3/\text{kg mol}^2) = a_o \exp(a_1 T + a_2 T^2)$

$b(\text{m}^3/\text{kg mol}) = b_o + b_1 T + b_2 T^2$

where temperature T is expressed in Kelvin

*ASHRAE values are a tabulation of correlated data and thus coefficients based on ASHRAE data must be considered provisional.

Table A.2. Coefficients for Curve-fit of Pure-Component Perfect-gas Heat Capacity

Refrigerant	c_0	c_1	$10^4 c_2$	Temp. Range of Data Fit (K)	Source
R11	22.0418	0.260895	-2.45319	200-400	JANAF
R12	17.5387	0.248546	-2.16271	200-400	JANAF
R13	13.9300	0.232181	-1.82929	200-400	JANAF
R13B1	19.9537	0.216394	-1.70241	200-400	JANAF
R14	11.0629	0.209740	-1.40992	200-400	JANAF
R22	17.0547	0.161633	-0.91256	200-400	JANAF
R23	20.4760	0.106183	-0.12189	200-400	JANAF
R113	76.2637	0.119641	0.71879	240-420	ASHRAE
R114	20.7005	0.464035	-4.17589	240-470	ASHRAE
R142b	23.7611	0.231706	-1.06534	250-500	Mears, et al.
R152a	22.2804	0.154009	-0.03067	200-400	Chen, et al.

NOTE: $C_P^o(\text{kJ/k mol K}) = c_0 + c_1 T + c_2 T^2$

where temperature T is expressed in Kelvin

Table A.3. Interaction Parameters for Refrigerant Mixtures

Mixture	Average f_{12}*	Standard Deviation in f_{12}*	Type of Data	No. Points	Temperature Range (K)	Composition Range	Source
R13B1/R152a	0.089	0.004	p_{sat} as $f(t,x_\ell)$	25	289-328	0.0-1.0	Morrison (1986)
R22/R12	0.041	0.009	N.B.P. as $f(x_\ell)$	21	232-239	0.0-1.0	Eiseman (1957)
R23/R13	0.089	0.010	p_{sat}, x_v as $f(T,x_\ell)$	69	200-273	0.0-1.0	Stein (1971)
R13/R12	0.035	0.010	p_{sat}, x_v as $f(T,x_\ell)$	17	255-290	0.0-1.0	Moluerup (1976)
R12/R152a	0.035	0.004	azeo. comp. as f(T)	4	243-313	0.55-0.65	Pennington (1952)
R22/R114	0.03	0.02	$psa_{t,}$, x_v as $f(T,x_\ell)$	36	253-333	0.10-0.91	Hackstein (1976)
R23/R12	0.088	0.020	p_{sat}, x_v as $f(T,x_\ell)$	36	193-273	0.0-1.0	Geller (1972)

*NOTE: A value of f_{12} was determined for each experimental data point, the average value is listed here. The standard deviation in the f_{12} values is an indication of the uncertainty in f_{12} arising from scatter in the experimental points and any temperature or composition dependence of f_{12}.

APPENDIX B: FORTRAN SUBROUTINES

This appendix contains listings of the FORTRAN subroutines developed to implement the equation of state for binary refrigerant mixtures as well as a sample run which uses the subroutines to compute a table of properties for an example mixture.

Notes on the use of these routines:

1) Language. All of the routines are written in ASCII standard FORTRAN (FORTRAN 77). Generic names are used for all calls to intrinsic functions (e.g., EXP and LOG).

2) Argument lists. Inputs and Outputs for each of the subroutines are described in comment statements at the beginning of each routine.

3) Units. The subroutines as presented here require all inputs and compute all outputs in SI units with the following multipliers:

   composition: mole fraction

   temperature: K

   volume: m^3/kg mol (equivalent to ℓ/g mol)

   pressure: kPa

   enthalpy: kJ/kg mol

   entropy, heat capacity and gas constant: kJ/kg mol K

   The routines will work with any other set of consistent units if the values of the gas constant and equation of state coefficients are converted in the BLOCK DATA routine. The user is reminded, however, that

English units (ft^3, psia, Btu, lb, etc.) are not consistent and would require insertion of conversion factors into each of the property subroutines.

4) Convergence tolerances and machine precision. The convergence tolerance for the iteration loops in the subroutines BUBLT and VIT are set by the value of TOLR in BLOCK DATA. The BUBLT routine contains nested iteration loops. As the calculation proceeds from the inner to outermost loop the convergence tolerance must be progressively relaxed; this is accomplished by scaling the convergence tolerance of each loop to a multiple of TOLR. A value of 10^{-7} is presently used for TOLR; this value worked well on a Sperry-Univac 1100/82 mainframe computer with a single precision word of 36 bits (approximately 8 decimal digits of accuracy) and a range of 10^{-38} to 10^{38}. This yielded a final precision of about one part in 10^5 for the calculation of saturation pressure. With a machine of lesser precision, a larger value of TOLR may be required. Greater precision can be obtained by reducing the value of TOLR but this may require converting the entire set of subroutines to double precision. (The programs are presented in single precision except for subroutine VIT.)

5) Warning messages. The logical unit to which any warning messages are written is currently set to 6 in the BLOCK DATA routine; this may be changed to suit different systems.

```
      SUBROUTINE FITAB (T,PE,VLE,VVE,WP,WL,WV,A,B,PC,VLC,VVC)
C
C   THIS SUBROUTINE CALCULATES THE 'A' AND 'B' PARAMETERS OF THE
C   EQUATION OF STATE WHICH BEST FITS A SET OF EXPERIMENTAL SATURATION
C   DATA FOR A PURE COMPONENT AT A GIVEN TEMPERATURE.  THE REQUIRED
C   DATA ARE SATURATION PRESSURE AND LIQUID AND VAPOR MOLAR
C   VOLUMES AT TEMPERATURE T.  WEIGHTING FACTORS ARE ASSOCIATED WITH
C   EACH EXPERIMENTAL QUANTITY AND MAY BE ADJUSTED TO ACCOUNT FOR THE
C   RELATIVE RELIABILITY OF THE VARIOUS EXPERIMENTAL QUANTITIES.  THE
C   INDIVIDUAL A AND B VALUES GIVEN BY THIS ROUTINE WOULD THEN BE FIT
C   BY A SEPARATE ROUTINE TO AN APPROPRIATE FUNCTION OF TEMPERATURE
C   FOR USE WITH THE EQUATION OF STATE.
C
C   INPUTS:
C      T - TEMPERATURE (K)
C      PE - EXPERIMENTAL SATURATION PRESSURE (KPA)
C      VLE - EXPERIMENTAL LIQUID PHASE MOLAR VOLUME (M**3/KMOL)
C      VVE - EXPERIMENTAL VAPOR VOLUME (M**3/KMOL)
C      WP - WEIGHTING FACTOR FOR PRESSURE DATA
C      WL - WEIGHTING FACTOR FOR LIQUID VOLUME DATA
C      WV - WEIGHTING FACTOR FOR VAPOR VOLUME DATA
C
C   OUTPUTS:
C      A - EQUATION OF STATE PARAMETER ASSOCIATED WITH INTERMOLECULAR
C          ATTRACTION (KJ M**3/KMOL**2)
C      B - EQUATION OF STATE PARAMETER ASSOCIATED WITH THE MOLECULAR
C          VOLUME (M**3/KMOL)
C      PC - SATURATION PRESSURE CALCULATED BY EQUATION OF STATE USING
C          ABOVE VALUES OF A AND B (KPA)
C      VLC - CALCULATED LIQUID VOLUME (M**3/KMOL)
C      VVC - CALCULATED VAPOR VOLUME (M**3/KMOL)
C
C   OTHER SUBROUTINES REFERENCED:
C      PLIMIT - DETERMINES INITIAL BOUNDS ON PRESSURE ITERATION
C      VIT - ITERATION FOR MOLAR VOLUME GIVEN T, P
C
C   NOTE:  IT IS NOT NECESSARY TO REFERENCE BCONST WHEN USING THIS
C      ROUTINE.  ALL NECESSARY COMMON BLOCKS ARE INITIALIZED HERE.
C      THE GAS CONSTANT IS SET (IN SI UNITS) IN THIS ROUTINE.
C
      IMPLICIT REAL (A-H,O-Z)
      COMMON /TOL/ TOLR,ITMAX,LUP
      COMMON /RDATA4/ R
      DIMENSION AA(2),BB(2),VL(2,2),VV(2,2),P(2,2),PG(3)
     1  ,PL(3),FP(2)
      LOGICAL LPPOS,LPNEG,LV1CON,LV2CON
C
C   STATEMENT FUNCTIONS FOR GIBBS FREE ENERGY AND THE DERIVATIVE
C   OF GIBBS FREE ENERGY WITH RESPECT TO THE B PARAMETER
C
      G(T,V,A,B)=R*T*(-LOG(V)+0.25*B/(V-0.25*B)**3
     1  *((8.0*V-2.25*B)*V+0.1875*B*B))+A/B*LOG(V/(V+B))-A/(V+B)
      DGDB(T,V,A,B)=R*T/(V-0.25*B)**3*((-2.25*V+0.375*B)+
     1  ((2.0*V-0.5625*B)*V+0.046875*B*B)*(V+0.5*B)/(V-0.25*B))+
     1  A*((1.0/(V+B)-ALOG(V/(V+B))/B)/B+1.0/(V+B)**2)
      R=8.314
      TOLR=1.0E-7
      ITMAX=20
      LUP=6
      PE2=PE*PE
      VLE2=VLE*VLE
      VVE2=VVE*VVE
      RT=R*T
C
C   USE EXPERIMENTAL LIQUID MOLAR VOLUME AS INITIAL GUESS FOR B AND
C   ENTER ITERATION TO FIND A, B WHICH EXACTLY SATISFY VOLUME DATA
C
      B=VLE
      DO 200 IT=1,100
      YL=0.25*B/VLE
```

```
      YV=0.25*B/VVE
      A=RT*((1.0+(1.0+(1.0-YL)*YL)*YL)/(VLE*(1.0-YL)**3)
     1  -(1.0+(1.0+(1.0-YV)*YV)*YV)/(VVE*(1.0-YV)**3))/
     1  (1.0/(VLE*(VLE+B))-1.0/(VVE*(VVE+B)))
      FG=G(T,VLE,A,B)-G(T,VVE,A,B)
      IF (ABS(FG).LT.TOLR) GOTO 240
      B2=B-FG/(DGDB(T,VLE,A,B)-DGDB(T,VVE,A,B))
      IF (B2.GT.4.0*VLE) B2=(B+4.0*VLE)/2.0
      IF (B2.LT.0.0) B2=0.5*B
      B=B2
  200 CONTINUE
  240 AA(2)=A
      BB(2)=B
      DO 260 I=2,1,-1
      DO 260 J=3-I,2
      VL(I,J)=VLE
  260 VV(I,J)=VVE
C
C   ENTER ITERATION TO FIND A, B WHICH BEST FIT P AND V DATA
C
      DO 400 IT=1,ITMAX
C
C   FIND VOLUMES AND PRESSURE PREDICTED BY EQUATION OF STATE FOR CURRENT
C   GUESS OF A, B AND FOR SLIGHTLY DIFFERENT A, B (FOR PURPOSES OF
C   NUMERICAL DIFFERENTIATION)
C
      AA(1)=1.001*AA(2)
      BB(1)=1.001*BB(2)
      DO 360 I=2,1,-1
      DO 360 J=3-I,2
C
C   CALL SUBROUTINE TO DETERMINE THE UPPER AND LOWER BOUNDS
C   ON PRESSURE FOR WHICH THERE ARE BOTH LIQUID AND VAPOR
C   SOLUTIONS OF THE EQUATION OF STATE
C
      CALL PLIMIT (T,AA(I),BB(J),VLOW,VUP,PLOW,PUP)
C
C   SET INITIAL GUESSES FOR PRESSURE NEAR THE UPPER AND
C   LOWER BOUNDS.  IF THE LOWER BOUND FOR PRESSURE IS NEGATIVE
C   RESET IT TO A SMALL POSITIVE VALUE.
C
      IF (PLOW.LE.0.0) THEN
        VLOW=0.8*BB(J)
        TC=AA(I)/(BB(J)*4.398909*R)
        PC=0.1049995*R*TC/BB(J)
        PLOW=1.0E-12*PC
        PG(1)=PLOW
      ELSE
        PG(1)=PLOW+0.0001*(PUP-PLOW)
      END IF
      PG(2)=PUP-0.0001*(PUP-PLOW)
      PL(1)=ALOG(PG(1))
      PL(2)=ALOG(PG(2))
      VL(I,J)=0.9*VLOW
      VV(I,J)=1.1*VUP
      KP=1
      LPPOS=.FALSE.
      LPNEG=.FALSE.
C
C   STARTING WITH INITIAL VALUES OF PRESSURE CLOSE TO THE UPPER
C   AND LOWER BOUNDS (FOUND BY SUBROUTINE PLIMIT) ITERATE ON
C   LOG (P) UNTIL THE GIBBS FREE ENERGY OF BOTH PHASES ARE EQUAL.
C   A COMBINATION OF SECANT AND REGULI-FALSI METHODS IS USED
C   FOR THE ITERATION.
C
C   ENTER ITERATION FOR SATURATION PRESSURE
C
      DO 300 ITP=1,ITMAX
      LV1CON=.FALSE.
      LV2CON=.FALSE.
```

```
C   EVALUATE VOLUMES FOR CURRENT VALUES OF A, B, P
      CALL VIT (T,PG(KP),AA(I),BB(J),VL(I,J),.TRUE.,LV1CON)
      CALL VIT (T,PG(KP),AA(I),BB(J),VV(I,J),.FALSE.,LV2CON)
C   PRESSURE ITERATION HAS CONVERGED WHEN GIBBS FREE ENERGY OF
C   LIQUID AND VAPOR PHASES ARE EQUAL
      FP(KP)=G(T,VL(I,J),AA(I),BB(J))-G(T,VV(I,J),AA(I),BB(J))
      IF (FP(KP).LT.0.0) THEN
        LPNEG=.TRUE.
        FPNEG=FP(KP)
        PNEG=PL(KP)
      ELSE
        LPPOS=.TRUE.
        FPPOS=FP(KP)
        PPOS=PL(KP)
      END IF
      IF (ITP.LE.1) THEN
        KP=2
      ELSE
        DGDPL=(FP(2)-FP(1))/(PL(2)-PL(1))
        IF (ABS(FP(KP)/(PL(KP)*DGDPL)).LT.TOLR) GOTO 340
C   NEXT GUESS FOR LOG (P) GIVEN BY SECANT METHOD
        PL(3)=PL(2)-FP(2)/DGDPL
C   IF NEXT GUESS FOR LOG (P) IS FURTHER FROM SOLUTION THAN
C   PREVIOUS BEST GUESS, USE REGULI-FALSI METHOD FOR NEXT GUESS
        IF ((PL(3).GT.MAX(PNEG,PPOS) .OR.
     1    PL(3).LT.MIN(PNEG,PPOS)) .AND. LPNEG .AND. LPPOS)
     1    PL(3)=PPOS-FPPOS*(PPOS-PNEG)/(FPPOS-FPNEG)
        PL(1)=PL(2)
        PL(2)=PL(3)
        FP(1)=FP(2)
        PG(2)=EXP(PL(2))
      END IF
  300 CONTINUE
  340 CONTINUE
      P(I,J)=PG(KP)
  360 CONTINUE
C
C   EVALUATE DERIVATIVE OF LIQUID AND VAPOR VOLUMES AND SATURATION
C   PRESSURE WITH RESPECT TO THE A AND B PARAMETERS AND SOLVE SYSTEM
C   OF EQUATIONS TO ARRIVE AT NEW GUESSES FOR A, B
C
      DA=AA(2)-AA(1)
      DB=BB(2)-BB(1)
      DVLDA=(VL(2,2)-VL(1,2))/DA
      DVLDB=(VL(2,2)-VL(2,1))/DB
      DVVDA=(VV(2,2)-VV(1,2))/DA
      DVVDB=(VV(2,2)-VV(2,1))/DB
      DPDA=(P(2,2)-P(1,2))/DA
      DPDB=(P(2,2)-P(2,1))/DB
      Q11=WL*(DVLDA/VLE)**2+WV*(DVVDA/VVE)**2+WP*(DPDA/PE)**2
      Q12=WL*DVLDA*DVLDB/VLE2+WV*DVVDA*DVVDB/VVE2+WP*DPDA*DPDB/PE2
      Q22=WL*(DVLDB/VLE)**2+WV*(DVVDB/VVE)**2+WP*(DPDB/PE)**2
      C1=WL*DVLDA*(VL(2,2)-VLE)/VLE2+WV*DVVDA*(VV(2,2)-VVE)/VVE2+
     1  WP*DPDA*(P(2,2)-PE)/PE2
      C2=WL*DVLDB*(VL(2,2)-VLE)/VLE2+WV*DVVDB*(VV(2,2)-VVE)/VVE2+
     1  WP*DPDB*(P(2,2)-PE)/PE2
      DET=Q11*Q22-Q12*Q12
      DELA=(C1*Q22-C2*Q12)/DET
      DELB=(C2*Q11-C1*Q12)/DET
      IF (ABS(DELA).GT. 0.2*ABS(AA(2))) THEN
        AA(2)=AA(2)-0.2*SIGN(AA(2),DELA)
      ELSE
        AA(2)=AA(2)-DELA
      END IF
      IF (ABS(DELB).GT. 0.2*ABS(BB(2))) THEN
        BB(2)=BB(2)-0.2*SIGN(BB(2),DELB)
      ELSE
        BB(2)=BB(2)-DELB
      END IF
C   ITERATION HAS CONVERVED WHEN SUCCESSIVE GUESSES FOR A AND B
```

```
C   ARE WITHIN A CONVERGENCE TOLERANCE.
      IF (ABS(DELA/AA(2)).LT.10.0*TOLR .AND.
     1  ABS(DELB/BB(2)).LT.10.0*TOLR) THEN
        A=AA(2)
        B=BB(2)
        PC=P(2,2)
        VLC=VL(2,2)
        VVC=VV(2,2)
        RETURN
      END IF
  400 CONTINUE
      WRITE (LUP,1200)
      A=AA(2)
      B=BB(2)
      PC=P(2,2)
      VLC=VL(2,2)
      VVC=VV(2,2)
      RETURN
 1200 FORMAT (1X,'ITERATION FOR A AND B DID NOT CONVERGE')
      END
```

```
 1        SUBROUTINE FITF (T,XL,PE,VLE,VVE,XVE,WP,WL,WV,WX,F,PC,VLC,
 2       1  VVC,XVC)
 3 C
 4 C    THIS ROUTINE DETERMINES THE INTERACTION PARAMETER WHICH BEST FITS
 5 C    A SET OF EXPERIMENTAL SATURATION DATA AT A GIVEN TEMPERATURE AND
 6 C    LIQUID COMPOSITION.  THE INDIVIDUAL VALUES OF THE INTERACTION
 7 C    PARAMETER DETERMINED BY THIS SUBROUTINE MAY THEN BE AVERAGED OVER
 8 C    MULTIPLE DATA SETS OR FIT AS A FUNCTION OF TEMPERATURE EITHER
 9 C    MANUALLY OR IN THE CALLING PROGRAM.  WEIGHTING FACTORS ARE
10 C    ASSOCIATED WITH EACH EXPERIMENTAL QUANTITY.  IF A PARTICULAR
11 C    QUANTITY IS UNAVAILABLE, THE CORRESPONDING WEIGHTING FACTOR SHOULD
12 C    BE SET TO ZERO.  A MINIMUM OF ONE MEASURED QUANTITY (IN ADDITION TO
13 C    TEMPERATURE AND LIQUID COMPOSITION) IS REQUIRED FOR THE
14 C    DETERMINATION OF THE INTERACTION PARAMETER.
15 C
16 C    INPUTS:
17 C       T - TEMPERATURE (K)
18 C       XL - LIQUID PHASE COMPOSITION (MOLE FRACTION)
19 C       PE - EXPERIMENTAL SATURATION PRESSURE (KPA)
20 C       VLE - EXPERIMENTAL LIQUID MOLAR VOLUME (M**3/KMOL)
21 C       VVE - EXPERIMENTAL VAPOR MOLAR VOLUME (M**3/KMOL)
22 C       XVE - EXPERIMENTAL VAPOR PHASE VOMPOSITION (MOL FRAC)
23 C       WP - WEIGHTING FACTOR FOR PRESSURE DATA
24 C       WL - WEIGHTING FACTOR FOR LIQUID VOLUME DATA
25 C       WV - WEIGHTING FACTOR FOR VAPOR VOLUME DATA
26 C       WX - WEIGHTING FACTOR FOR VAPOR COMPOSITION DATA
27 C
28 C    OUTPUTS:
29 C       F - VALUE OF THE INTERACTION PARAMETER WHICH BEST FIT THE
30 C          EXPERIMENTAL DATA (DIMENSIONLESS)
31 C       PC - SATURATION PRESSURE CALCULATED BY EQUATION OF STATE
32 C          USING ABOVE VALUE OF F (KPA)
33 C       VLC - CALCULATED LIQUID VOLUME (M**3/KMOL)
34 C       VVC - CALCULATED VAPOR VOLUME (M**3/KMOL)
35 C       XVC - CALCULATED VAPOR COMPOSITION (MOL FRAC)
36 C
37 C    OTHER SUBROUTINES REFERENCED:
38 C       ESPAR - COMPUTATION OF EQUATION OF STATE PARAMETERS
39 C       BUBLT - CALCULATE SATURATION CONDITIONS AT GIVEN T, XL
40 C       BUBLT IN TURN REFERENCES:
41 C       PLIMIT - DETERMINES INITIAL BOUNDS ON PRESSURE ITERATION
42 C       VIT - ITERATION FOR MOLAR VOLUME GIVEN T, P
43 C       ZXLSF - ONE-DIMENSIONAL MINIMIZATION ROUTINE CONTAINED IN
44 C          PROPRIETARY IMSL MATH/STATISTICS LIBRARY.  AN
45 C          EQUVILENT ROUTINE FROM THE USER'S COMPUTER CENTER
46 C          MAY BE USED BY MODIFYING LINES 69 - 85 AND THE EXTERNAL
47 C          FUNCTION SFUNC AS APPROPRIATE.
48 C
49 C    NOTE:  THE SUBROUTINE BCONST MUST BE CALLED ONCE BY THE MAIN
50 C       PROGRAM FOR EACH MIXTURE UNDER CONSIDERATION
51 C
52 C    COMMON BLOCK DPASS IS USED TO PASS INFORMATION TO THE EXTERNAL
53 C    FUNCTION SFUNC WHICH CALCULATED THE EXPRESSION TO BE MINIMIZED.
54 C
55        COMMON /DPASS/ TP,XLP,PEP,VLEP,VVEP,XVEP,WPP,WLP,WVP,WXP,
56       1  PCP,VLCP,VVCP,XVCP
57        EXTERNAL SFUNC
58        DATA STEP/0.004/,SBOUND/0.4/,SACC/1.0E-6/,MAXFN/40/
59 C   FILL UP COMMON BLOCK FROM ARGUMENT LIST OF SUBROUTINE
60        TP=T
61        XLP=XL
62        PEP=PE
63        VLEP=VLE
64        VVEP=VVE
65        XVEP=XVE
66        WPP=WP
67        WLP=WL
68        WVP=WV
69        WXP=WX
70        F=0.04
```

```
      IERR=0
C
C   PARAMETERS FOR THE MINIMIZATION ROUTINE:
C      SFUNC - EXTERNAL FUNCTION SUBROUTINE WHICH EVALUATES THE
C              EXPRESSION TO BE MINIMZED AS A FUNCTION OF F
C      F - VALUE OF THE INDEPENDENT VARIABLE (IN THIS CASE THE
C          INTERACTION PARAMETER) WHICH MINIMIZES SFUNC
C      STEP - INITIAL INCREMENT BY WHICH TO  CHANGE F IN THE ITERATION
C             TO FIND MINIMUM
C      SBOUND - MAXIMUM AMOUNT THAT F CAN BE VARIED ABOVE OR BELOW
C               INITIAL VALUE
C      SACC - ABSOLUTE ACCURACY TO WHICH F IS TO BE DETERMINED
C      MAXFN - MAXIMUM NUMBER OF ALLOWED CALLS TO SFUNC
C      IERR - ERROR FLAG; A VALUE > 128 INDICATES AN ERROR
C
      CALL ZXLSF (SFUNC,F,STEP,SBOUND,SACC,MAXFN,IERR)
C
C   TRANSFER CALCULATED QUANTITES FROM COMMON BLOCK
C
      PC=PCP
      VLC=VLCP
      VVC=VVCP
      XVC=XVCP
      END
C
C
      FUNCTION SFUNC (F)
C
C   THIS FUNCTION EVALUATES THE SUM OF SQUARES DEVIATION BETWEEN
C   THE EXPERIMENTAL AND CALCULATED QUANTITIES
C
      LOGICAL LCRIT,LTRUE
      COMMON /DPASS/ TP,XLP,PE,VLE,VVE,XVE,WP,WL,WV,WX,
     1  PCP,VLCP,VVCP,XVCP
      COMMON /RDATA1/ AA0,AA1,AA2,AB0,AB1,AB2,BA0,BA1,BA2,
     1  BB0,BB1,BB2,F0,F1
      LTRUE=.TRUE.
      F0=F
      T=TP
      XL=XLP
C
C   CALL SUBROUTINE ESPAR TO REEVALUATE A, B PARAMTERS USING CURRENT
C   GUESS FOR F
C
      CALL ESPAR (-1,T,XL,A,B)
C   COMPUTE SATURATION PROPERTIES AT GIVEN T, XL
      CALL BUBLT (T,XL,XVC,PC,VLC,VVC,LTRUE,LCRIT)
      SFUNC=WP*((PE-PC)/PC)**2+WL*((VLE-VLC)/VLC)**2+
     1  WV*((VVE-VVC)/VVC)**2+WX*(XVE-XVC)**2
      PCP=PC
      VLCP=VLC
      VVCP=VVC
      XVCP=XVC
      RETURN
      END
```

```
      SUBROUTINE BCONST (IR1,IR2,F0,F1)
C
C   THIS ROUTINE ACCESSES THE CURVE FIT COEFFICIENTS TO THE EQUATION
C   OF STATE PARAMETERS (STORED IN BLOCK DATA BDESC) FOR THE
C   REFRIGERANT PAIR OF INTEREST.  THE REFERENCE STATES FOR ENTHALPY
C   AND ENTROPY ARE ALSO COMPUTED.  THIS SUBROUTINE MUST BE CALLED
C   BEFORE ANY OTHER PROPERTY ROUTINES ARE REFERENCED AND ALSO IF
C   THE MIXTURE OR THE VALUES OF THE INTERACTION COEFFICIENTS F0, F1
C   ARE CHANGED.
C
C   INPUTS:
C      IR1, IR2 - CODE NUMBERS FOR PURE COMPONENTS
C      F0, F1 - COEFFICIENTS TO THE CURVE FIT FOR THE INTERACTION
C               PARAMETER:  F = F0 + F1*T
C
C   OUTPUTS (VIA COMMON BLOCKS):
C      A - ARRAY OF A COEFFICIENTS FOR THE TWO PURE COMPONENTS
C      B - ARRAY OF B COEFFICIENTS FOR THE PURE COMPONENTS
C      CP - ARRAY OF PURE COMPONENT CP0 COEFFICIENTS
C      HR - TWO ELEMENT ARRAY OF PURE COMPONENT REFERENCE
C        ENTHALPIES; THESE ARE EQUAL TO THE SATURATED LIQUID
C        ENTHALPY AT THE REFERENCE TEMPERATURE MINUS THE PERFECT
C        GAS ENTHALPY AT THE REFERENCE TEMPERATURE
C      SR - REFERENCE ENTROPIES; EQUAL TO THE DIFFERENCE BETWEEN
C        THE SATURATED LIQUID AND PERFECT GAS ENTROPIES AT THE
C        REFERENCE TEMPERATURE
C      TC - PURE COMPONENT CRITICAL TEMPERATURES
C      TREF - REFERENCE TEMPERATURES AT WHICH HR AND SR ARE COMPUTED
C      WM - PURE COMPONENT MOLECULAR WEIGHTS
C
C   OTHER SUBROUTINES REFERENCED:
C      BUBLT - COMPUTE SATURATED LIQUID AND VAPOR CONDITIONS
C      HCVCP - COMPUTE ENTHALPY AT REFERENCE STATE
C      ENTROP - COMPUTE REFERENCE ENTROPY
C
      IMPLICIT REAL (A-H,O-Z)
      DIMENSION COEFF(9,20),CRIT(5,20),WM(2),TC(2),A(3,2),B(3,2),
     1  CP(3,2),HR(2),SR(2),VR(2),TREF(2),HZERO(20),SZERO(20)
      INTEGER IR(2)
      CHARACTER*6 HREF(20)
      COMMON /ESDATA/ COEFF,CRIT
      COMMON /HREF1/ HREF
      COMMON /RDATA1/ A,B,FF0,FF1
      COMMON /RDATA2/ WM,TC
      COMMON /CPDATA/ CP
      COMMON /REF/ TREF,HR,SR,VR
      COMMON /HSZERO/ HZERO,SZERO
      IR(1)=IR1
      IR(2)=IR2
      IR1=ABS(IR1)
      IR2=ABS(IR2)
      FF0=F0
      FF1=F1
      DO 100 KR=1,2
      IF (IR(KR).GT.0) THEN
C   IF IR IS NEGATIVE READ IN COEFFICIENTS FROM DATA FILE
      ELSE IF (IR(1).EQ.ABS(IR(2)) .AND. KR.EQ.2) THEN
        HREF(IR1)=HREF(IR2)
        DO 66 KC=1,5
   66   CRIT(KC,IR2)=CRIT(KC,IR1)
        HZERO(IR2)=HZERO(IR1)
        SZERO(IR2)=SZERO(IR1)
        DO 68 KC=1,9
   68   COEFF(KC,IR2)=COEFF(KC,IR1)
      ELSE
        IRK=ABS(IR(KR))
        READ (*,1000) HREF(IRK)
        READ (*,*) (CRIT(KC,IRK),KC=1,5),
     1    HZERO(IRK),SZERO(IRK),
     1    (COEFF(KC,IRK),KC=1,9)
```

```
      END IF
      IR(KR)=ABS(IR(KR))
      WM(KR)=CRIT(1,IR(KR))
      TREF(KR)=CRIT(2,IR(KR))
      TC(KR)=CRIT(3,IR(KR))
      HR(KR)=0.0
      SR(KR)=0.0
      DO 100 KC=1,3
      A(KC,KR)=COEFF(KC,IR(KR))
      B(KC,KR)=COEFF(KC+3,IR(KR))
  100 CP(KC,KR)=COEFF(KC+6,IR(KR))
      CALL ESPAR (-2,TREF(1),0.0,AB,BB)
C
C   CALL BUBBLE POINT ROUTINE TO CALCULATE SATURATED LIQUID AND VAPOR
C   VOLUMES AND THEN CALL ENTHALPY AND ENTROPY ROUTINE TO DETERMINE
C   REFERENCE VALUES.  THE HZERO AND SZERO ALLOW AN ARBITRARY VALUE
C   TO BE ASSIGNED TO THE SATURATED LIQUID H OR S AT THE REFERENCE
C   TEMPERATURE.
C
      CALL BUBLT (TREF(1),1.0,XV,P,VR(1),VV,.TRUE.,.FALSE.)
      CALL BUBLT (TREF(2),0.0,XV,P,VR(2),VV,.TRUE.,.FALSE.)
      DO 160 I=1,2
      XL=FLOAT(2-I)
      CALL HCVCP (1,TREF(I),VR(I),XL,HR(I),CV,XCP)
      HR(I)=HR(I)-HZERO(IR(I))
      SR(I)=ENTROP(TREF(I),VR(I),XL)-SZERO(IR(I))
  160 CONTINUE
      RETURN
 1000 FORMAT (A6)
      END
```

```
      SUBROUTINE BUBLT (T,XL,XV,P,VL,VV,LBUB,LCRIT)
C
C   GIVEN TEMPERATURE AND COMPOSITION OF ONE PHASE THIS ROUTINE
C   CALCULATES THE SATURATION PRESSURE, THE COMPOSITION OF THE OTHER
C   PHASE AND THE LIQUID AND VAPOR MOLAR VOLUMES.
C
C   INPUTS:
C      T - TEMPERATURE (K)
C      ONLY ONE OF:  XL - LIQUID COMPOSITION (MOLE FRACTION)
C                OR:  XV - VAPOR COMPOSITION (MOLE FRACTION)
C      LBUB - LOGICAL VARIABLE
C         IF LBUB=.TRUE. LIQUID COMPOSITION IS GIVEN (COMPUTE
C         BUBBLE POINT)
C         IF LBUB=.FALSE. VAPOR COMPOSITION IS GIVEN (COMPUTE
C         DEW POINT)
C
C   OUTPUTS:
C      XL OR XV - COMPOSITION OF CALCULATED PHASE
C      P - SATURATION PRESSURE (KPA)
C      VL - LIQUID MOLAR VOLUME (M**3/KMOL)
C      VV - VAPOR MOLAR VOLUME (M**3/KMOL)
C      LCRIT - ERROR FLAG; IF LCRIT=.TRUE. THE INPUT TEMPERATURE
C         EXCEEDS THE CRITICAL TEMPERATURE OF THE PURE COMPONENT
C         OR THE PSEUDO-PURE COMPONENT CORRESPONDING TO THE
C         MIXTURE COMPOSITION AND NO CALCULATIONS ARE DONE.
C
C   OTHER SUBROUTINES REFERENCED:
C      VIT - ITERATION FOR MOLAR VOLUME
C      PLIMIT - DETERMINES INITIAL BOUNDS ON PRESSURE AND VOLUME
C      ESPAR - COMPUTATION OF EQUATION OF STATE PARAMETERS
C
C   GENERAL NOMENCLATURE FOR FIRST LETTER OF VARIABLE NAMES
C      A,B - EQUATION OF STATE PARAMETERS
C      F - MIXING PARAMETER
C      T - TEMPERATURE
C      P - PRESSURE
C      V - MOLAR VOLUME
C      X - COMPOSITION
C      G - GIBBS FREE ENERGY
C      U - CHEMICAL POTENTIAL
C      Y - COMBINATION OF VARIABLES USED IN EQUATION OF STATE
C      TOL - CONVERGENCE TOLERANCE FOR ITERATION LOOPS
C      I,J - INDEX VARIABLES FOR ITERATION AND DO LOOPS
C      L - LOGICAL VARIABLES SUCH AS NON-CONVERGENCE FLAGS
C
C   GENERAL NOMENCLATURE FOR SECOND OR THIRD LETTER OF VARIABLES
C      A,B - COMPONENTS OF MIXTURE; COMPOSITION IS MOLE FRACTION A
C      L - LIQUID PHASE
C      V - VAPOR PHASE
C      1 - PARENT PHASE (PHASE WITH SPECIFIED COMPOSITION)
C      2 - INCIPIENT PHASE
C      (FOR EXAMPLE UA1 REFERS TO CHEMICAL POTENTIAL OF COMPONENT A
C      IN PHASE 1)
C
C
      IMPLICIT REAL (A-H,O-Z)
      LOGICAL LBUB,LCRIT,LV1CON,LV2CON,LXCON,LXPOS,LXNEG,
     1  LPPOS,LPNEG,LPPCON
      COMMON /ESPAR1/ AA,AB,BA,BB,F,C1,D1,C2,D2
      COMMON /RDATA4/ R
      COMMON /TOL/ TOLR,ITMAX,LUP
      DIMENSION PP(3),FP(2),XX2(3),FX2(2),PL(3)
C
C   STATEMENT FUNCTIONS FOR GIBBS FREE ENERGY AND CHEMICAL POTENTIAL
C   NOTE THAT SINCE ONLY DIFFERENCES OF G AND U ARE USED IN THE PROGRAM
C   ANY TERMS WHICH WOULD CANCEL ARE OMITTED.  THE EXPRESSION FOR U
C   IS DIVIDED BY RT TO OBTAIN A DIMENSIONLESS QUANTITY.
C
      G(T,V,A,B)=R*T*(-LOG(V)+0.25*B*((8.0*V-2.25*B)*V+0.1875*B*B)
     1  /(V-0.25*B)**2/(V-0.25*B))+A/B*LOG(V/(V+B))-A/(V+B)
```

```
      U(T,X,V,A,B,AA,AB,BI,F,Y)=(Y*(4.0-3.0*Y)+BI*(4.0-2.0*Y)*Y/
     1  (B*(1.0-Y)))/(1.0-Y)**2+(BI*A*LOG(1.0+B/V)/B-BI*A/(V+B)
     1  +2.*(X*AA+(1.0-F)*(1.0-X)*SQRT(AA*AB))*LOG(V/(V+B)))/(R*T*B)
     1  -LOG(V)
C
      LCRIT=.FALSE.
C
C   COMPUTE PURE COMPONENT E.S. COEFFICIENTS, THE MIXING PARAMETER,
C   AND THE E.S. COEFFICIENTS FOR PHASE 1
C
      IF (LBUB) THEN
        X1=XL
        XV=XL
      ELSE
        X1=XV
        XL=XV
      END IF
      XB1=1.0-X1
      CALL ESPAR (0,T,X1,A1,B1)
C
C   DETERMINE IF INPUT TEMPERATURE EXCEEDS CRITICAL POINT;
C   IF SO, SET ERROR FLAG AND RETURN
C
      TC=A1/(B1*4.398909*R)
      IF (T.GT.0.99*TC) THEN
        LCRIT=.TRUE.
        WRITE (LUP,1010)
        RETURN
      END IF
C
C   ENTER ITERATION FOR PSEUDO-PURE COMPONENT.  THIS ITERATION
C   YIELDS THE FINAL RESULT FOR A PURE COMPONENT AND PROVIDES
C   A STARTING GUESS FOR THE PRESSURE OF A MIXTURE
C
C   CALL SUBROUTINE TO DETERMINE THE UPPER AND LOWER BOUNDS
C   ON PRESSURE FOR WHICH THERE ARE BOTH LIQUID AND VAPOR
C   SOLUTIONS OF THE EQUATION OF STATE
C
      CALL PLIMIT (T,A1,B1,VLOW,VUP,PLOW,PUP)
C
C   SET INITIAL GUESSES FOR PRESSURE NEAR THE UPPER AND
C   LOWER BOUNDS.  IF THE LOWER BOUND FOR PRESSURE IS NEGATIVE
C   RESET IT TO A SMALL POSITIVE VALUE.
C
      IF (PLOW.LE.0.0) THEN
        VLOW=0.8*B1
        PC=0.1049995*R*TC/B1
        PLOW=1.0E-12*PC
        PP(1)=PLOW
      ELSE
        PP(1)=PLOW+0.0001*(PUP-PLOW)
      END IF
      PP(2)=PUP-0.0001*(PUP-PLOW)
      PL(1)=LOG(PP(1))
      PL(2)=LOG(PP(2))
      VL=0.9*VLOW
      VV=1.1*VUP
      J=1
      LPPOS=.FALSE.
      LPNEG=.FALSE.
      LPPCON=.FALSE.
C
C   STARTING WITH INITIAL VALUES OF PRESSURE CLOSE TO THE UPPER
C   AND LOWER BOUNDS (FOUND BY SUBROUTINE PLIMIT) ITERATE ON
C   LOG (P) UNTIL THE GIBBS FREE ENERGY OF BOTH PHASES ARE EQUAL.
C   A COMBINATION OF SECANT AND REGULI-FALSI METHODS IS USED
C   FOR THE ITERATION.
C
      DO 400 IT=1,ITMAX
      LV1CON=.FALSE.
```

```
      LV2CON=.FALSE.
      CALL VIT (T,PP(J),A1,B1,VL,.TRUE.,LV1CON)
      CALL VIT (T,PP(J),A1,B1,VV,.FALSE.,LV2CON)
      GL=G(T,VL,A1,B1)
      GV=G(T,VV,A1,B1)
      FP(J)=GL-GV
      IF (FP(J).LT.0.0) THEN
        LPNEG=.TRUE.
        FPNEG=FP(J)
        PNEG=PL(J)
      ELSE
        LPPOS=.TRUE.
        FPPOS=FP(J)
        PPOS=PL(J)
      END IF
      IF (IT.LE.1) THEN
        J=2
      ELSE
        DGDPL=(FP(2)-FP(1))/(PL(2)-PL(1))
        IF (DGDPL.EQ.0.0) GOTO 440
        IF (ABS(FP(J)/(PL(J)*DGDPL)).LT.TOLR) GOTO 440
C   NEXT GUESS FOR LOG (P) GIVEN BY SECANT METHOD
        PL(3)=PL(2)-FP(2)/DGDPL
C   IF NEXT GUESS FOR LOG (P) IS FURTHER FROM SOLUTION THAN
C   PREVIOUS BEST GUESS, USE REGULI-FALSI METHOD FOR NEXT GUESS
        IF ((PL(3).GT.MAX(PNEG,PPOS) .OR.
     1    PL(3).LT.MIN(PNEG,PPOS)) .AND. LPNEG .AND. LPPOS)
     1    PL(3)=PPOS-FPPOS*(PPOS-PNEG)/(FPPOS-FPNEG)
        PL(1)=PL(2)
        PL(2)=PL(3)
        FP(1)=FP(2)
        PP(2)=EXP(PL(2))
      END IF
  400 CONTINUE
C   IF ITERATION HAS NOT CONVERGED, SET ERROR FLAG.
      LPPCON=.TRUE.
C
C   END OF PSEUDO-PURE COMPONENT ITERATION
C
C   FOR A PURE COMPONENT THE ABOVE ITERATION GIVES THE FINAL RESULT
C
  440 IF (X1*XB1.LE.TOLR) THEN
        IF (LV1CON) WRITE (LUP,1050)
        IF (LV2CON) WRITE (LUP,1055)
        IF (LPPCON) WRITE (LUP,1020)
        P=PP(J)
        RETURN
      END IF
C
C   ENTER ITERATION FOR MIXTURE
C
C   THE MIXTURE ITERATION CONSISTS OF TWO CONCENTRIC ITERATION
C   LOOPS WHICH VARY THE SATURATION PRESSURE OF THE MIXTURE AND THE
C   COMPOSITION OF THE COMPUTED PHASE TO GIVE EQUAL CHEMICAL
C   POTENTIALS FOR EACH OF THE COMPONENTS BETWEEN THE TWO PHASES.
C   THE INITIAL GUESS FOR THE PRESSURE IS GIVEN BY THE PSEUDO-PURE
C   ITERATION ABOVE; THE INITIAL GUESS FOR COMPOSITION IS THAT X2=X1.
C
C   ASSIGN INITIAL VALUES OF LIQUID AND VAPOR VOLUMES FROM ABOVE
C   ITERATION TO PHASE 1 AND 2 VOLUMES.
C
      IF (LBUB) THEN
        V1=VL
        V2=VV
      ELSE
        V1=VV
        V2=VL
      END IF
      PP(1)=PP(J)
C
```

```
C   BEGIN ITERATION FOR SATURATION PRESSURE OF MIXTURE
C
      J=1
      X2CONV=X1
      LPNEG=.FALSE.
      LPPOS=.FALSE.
      DO 800 ITP=1,ITMAX
      XX2(1)=X2CONV
      LXCON=.FALSE.
      LV1CON=.FALSE.
      CALL VIT (T,PP(J),A1,B1,V1,LBUB,LV1CON)
C
C   IF VOLUME ITERATION HAS NOT CONVERGED, TRY A NEW PRESSURE AND
C   RETURN TO THE BEGINNING OF THE ITERATION
C
      IF (LV1CON .OR. LXCON) THEN
        PP(2)=0.5*(PP(1)+PP(2))
        GOTO 800
      END IF
C   COMPUTE CHEMICAL POTENTIALS FOR PHASE 1
      Y=0.25*B1/V1
      UA1=U(T,X1,V1,A1,B1,AA,AB,BA,F,Y)
      UB1=U(T,XB1,V1,A1,B1,AB,AA,BB,F,Y)
C
C   ENTER INNER ITERATION LOOP (FOR COMPOSITION OF PHASE 2)
C
      JJ=1
      LXNEG=.FALSE.
      LXPOS=.FALSE.
      DO 600 IT=1,ITMAX
      LV2CON=.FALSE.
      XB2=1.0-XX2(JJ)
C   COMPUTE EQUATION OF STATE COEFFICIENTS FOR PHASE 2
      CALL ESPAR (0,T,XX2(JJ),A2,B2)
      CALL VIT (T,PP(J),A2,B2,V2,.NOT.LBUB,LV2CON)
C
C   IF VOLUME ITERATION HAS NOT CONVERGED, TRY A NEW PRESSURE
C   AND RETURN TO THE START OF THE PRESSURE ITERATION.
C
      IF (LV2CON) THEN
        PP(2)=0.5*(PP(1)+PP(2))
        GOTO 800
      END IF
C  COMPUTE CHEMICAL POTENTIALS OF PHASE 2
      Y=0.25*B2/V2
      UA2=U(T,XX2(JJ),V2,A2,B2,AA,AB,BA,F,Y)
      UB2=U(T,XB2,V2,A2,B2,AB,AA,BB,F,Y)
C
C   CALCULATE THE COMPOSITION OF PHASE 2 FROM THE COMPOSITION
C   OF PHASE 1 AND THE CHEMICAL POTENTIALS.  THE INNER ITERATION
C   LOOP HAS CONVERGED WHEN THE CALCULATED COMPOSITION EQUALS
C   (WITHIN A CONVERGENCE TOLERANCE) THE GUESSED VALUE OF X2.
C
      ZA=X1*EXP(UA1-UA2)
      ZB=XB1*EXP(UB1-UB2)
      C=ZA+ZB
      X2CALC=ZA/C
      FX2(JJ)=X2CALC-XX2(JJ)
      IF (ABS(FX2(JJ)).LT.TOLR) THEN
        X2CONV=XX2(JJ)
        GOTO 640
      END IF
C   UPDATE POSITIVE OR NEGATIVE BOUNDS FOR USE WITH REGULI-FALSI
      IF (FX2(JJ).LT.0.0) THEN
        LXNEG=.TRUE.
        FXNEG=FX2(JJ)
        XNEG=XX2(JJ)
      ELSE
        LXPOS=.TRUE.
        FXPOS=FX2(JJ)
```

```
281          XPOS=XX2(JJ)
282        END IF
283 C
284 C   UPDATE THE GUESS FOR X2.  THE COMPOSITION COMPUTED ABOVE IS
285 C   USED FOR THE SECOND GUESS.  A COMBINATION OF SECANT AND
286 C   REGULI-FALSI METHODS IS USED FOR THIRD AND SUBSEQUENT GUESSES.
287 C
288        IF (IT.LE.1) THEN
289          JJ=2
290          XX2(2)=X2CALC
291        ELSE
292          IF (FX2(1).EQ.FX2(2)) THEN
293            X2CONV=XX2(JJ)
294            GOTO 640
295          END IF
296          XX2(3)=XX2(2)-FX2(2)*(XX2(2)-XX2(1))/(FX2(2)-FX2(1))
297          IF (LXPOS .AND. LXNEG) THEN
298          IF (XX2(3).LT.MIN(XPOS,XNEG) .OR. XX2(3).GT.MAX(XPOS,XNEG)) THEN
299              XX2(3)=XPOS-FXPOS*(XPOS-XNEG)/(FXPOS-FXNEG)
300            END IF
301          END IF
302          XX2(1)=XX2(2)
303          XX2(2)=XX2(3)
304          FX2(1)=FX2(2)
305        END IF
306        XX2(JJ)=MIN(1.0,MAX(0.0,XX2(JJ)))
307    600 CONTINUE
308 C   IF INNER ITERATION LOOP HAS NOT CONVERGED, SET ERROR FLAG
309        LXCON=.TRUE.
310 C
311 C   END OF ITERATION LOOP FOR PHASE 2 COMPOSITION
312 C
313    640 FP(J)=1.0-C
314 C
315 C   OUTER (PRESSURE) ITERATION HAS CONVERGED WHEN C = 1.000
316 C   (I.E. WHEN THE CHEMICAL POTENTIALS OF EACH COMPONENT ARE
317 C   THE SAME IN BOTH PHASES).
318 C
319        IF (ABS(FP(1)).LT.100.*TOLR) GOTO 840
320 C
321 C   PROVIDED THAT THE X2 ITERATION HAS CONVERGED FOR THE CURRENT
322 C   GUESS OF PRESSURE, UPDATE THE POSITIVE AND NEGATIVE
323 C   BOUNDS FOR USE WITH THE REGULI-FALSI METHOD.
324 C
325        IF (.NOT.LXCON) THEN
326          IF (FP(J).LT.0.0) THEN
327            LPNEG=.TRUE.
328            FPNEG=FP(J)
329            PNEG=PP(J)
330          ELSE
331            LPPOS=.TRUE.
332            FPPOS=FP(J)
333            PPOS=PP(J)
334          END IF
335        END IF
336 C
337 C   COMPUTE NEW GUESS FOR SATURATION PRESSURE.
338 C
339        IF (ITP.LE.2 .OR. FP(1).EQ.FP(2)) THEN
340          PP(1)=PP(J)
341          FP(1)=FP(J)
342          IF (LBUB) THEN
343            PP(2)=PP(J)*C
344          ELSE
345            PP(2)=PP(J)/C
346          END IF
347          J=2
348        ELSE
349          PP(3)=PP(2)-FP(2)*(PP(2)-PP(1))/(FP(2)-FP(1))
350          IF ((PP(3).GT.MAX(PNEG,PPOS) .OR.
```

```
     1    PP(3).LT.MIN(PNEG,PPOS)) .AND. LPNEG .AND. LPPOS)
     1    PP(3)=PPOS-FPPOS*(PPOS-PNEG)/(FPPOS-FPNEG)
        PP(1)=PP(2)
        PP(2)=PP(3)
        FP(1)=FP(2)
      END IF
  800 CONTINUE
      WRITE (LUP,1040)
  840 P=PP(J)
C
C   ASSIGN RESULTS FOR PHASES 1 AND 2 TO LIQUID AND VAPOR PHASES
C   DEPENDING ON WHETHER THE DEW OR BUBBLE POINT WAS CALCULATED.
C
      IF (LBUB) THEN
        XV=XX2(JJ)
        VL=V1
        VV=V2
      ELSE
        XL=XX2(JJ)
        VL=V2
        VV=V1
      END IF
C
C   PRINT WARNING MESSAGES FOR ANY CASES OF NON-CONVERGENCE OCCURING
C   ON FINAL CALL TO EACH ITERATION AND RETURN.
C
      IF (LV1CON) WRITE (LUP,1050)
      IF (LV2CON) WRITE (LUP,1055)
      IF (LXCON) WRITE (LUP,1060)
      RETURN
 1010 FORMAT (1X,'CRITICAL POINT OF PURE OR PSEUDO-PURE MATERIAL',
     1  ' EXCEEDED IN BUBLT')
 1020 FORMAT (1X,'PURE MATERIAL PRESSURE ITERATION IN BUBLT',
     1  ' DID NOT CONVERGE')
 1040 FORMAT (1X,'MIXTURE PRESSURE ITERATION IN BUBLT DID NOT',
     1  ' CONVERGE')
 1050 FORMAT (1X,'VOLUME ITERATION FOR PARENT PHASE DID',
     1  ' NOT CONVERGE')
 1055 FORMAT (1X,'VOLUME ITERATION FOR INCIPIENT PHASE DID',
     1  ' NOT CONVERGE')
 1060 FORMAT (1X,'COMPOSITION ITERATION IN BUBLT DID NOT CONVERGE')
      END
```

```
      FUNCTION ENTROP(T,V,X)
C
C   COMPUTE SPECIFIC ENTROPY OF A SINGLE PHASE TWO-COMPONENT MIXTURE
C   AS A FUNCTION OF TEMPERATURE, SPECIFIC VOLUME, AND COMPOSITION
C
C   INPUTS:
C      T - TEMPERATURE (K)
C      V - SPECIFIC VOLUME (M**3/KMOL)
C      X - COMPOSITION (MOLE FRACTION)
C
C   OUTPUT:
C      S - SPECIFIC ENTROPY (KJ/KMOL K)
C
C   OTHER SUBROUTINES REFERENCED BY ENTROP:
C      ESPAR - COMPUTATION OF EQUATION OF STATE PARAMETERS
C
C
      IMPLICIT REAL (A-H,O-Z)
      COMMON /ESPAR1/ AA,AB,BA,BB,F,C1,D1,C2,D2
      COMMON /REF/ TREFA,TREFB,HRA,HRB,SRA,SRB,VRA,VRB
      COMMON /CPDATA/ CPA0,CPA1,CPA2,CPB0,CPB1,CPB2
      COMMON /HSPURE/ HPA,HPB,SPA,SPB,CP0A,CP0B
      COMMON /RDATA4/ R
      CALL ESPAR (1,T,X,A,B)
      B4=0.25*B
      S=X*(SPA-SRA+R*LOG(V/VRA))+(1.0-X)*(SPB-SRB+R*LOG(V/VRB))
     1  +(C1*B-A*D1)/B**2*LOG((V+B)/V)+A*D1/B/(V+B)
     1  -R*B4/(V-B4)**2*(4.0*V-3*B4)
     1  -R*T*D1*0.5*V/(V-B4)**3*(2.0*V-B4)
      IF (X.GT.0.0 .AND. X.LT.1.0) THEN
        S=S-R*(X*LOG(X)+(1.0-X)*LOG(1.0-X))
      END IF
      ENTROP=S
      RETURN
      END
```

```
      SUBROUTINE HCVCP(IQ,T,V,X,H,CV,CP)
C
C   GIVEN TEMPERATURE, MOLAR VOLUME AND COMPOSITION COMPUTE ENTHALPY
C   AND/OR HEAT CAPACITY AT CONSTANT VOLUME AND/OR PRESSURE AS SPECIFIED
C   BY OUTPUT QUALIFIER IQ.  (SINGLE PHASE ONLY)
C
C   INPUTS:
C      IQ - OUTPUT QUALIFIER
C         = 1 COMPUTE ENTHALPY ONLY
C         = 2 ENTHALPY AND CONSTANT VOLUME HEAT CAPACITY
C         = 3 ENTHALPY AND HEAT CAPACITY AT CONSTANT VOLUME AND PRESSURE
C         = 4 COMPUTE HEAT CAPACITY AT CONSTANT VOLUME ONLY
C         = 5 HEAT CAPACITY AT CONSTANT VOLUME AND AT CONSTANT PRESSURE
C      T - TEMPERATURE (K)
C      V - MOLAR VOLUME (M**3/KMOL)
C      X - COMPOSITION (MOLE FRACTION)
C
C   OUTPUTS:
C      H - MOLAR ENTHALPY (KJ/KMOL)
C      CV - HEAT CAPACITY AT CONSTANT VOLUME (KJ/KMOL K)
C      CP - HEAT CAPACITY AT CONSTANT PRESSURE (KJ/KMOL K)
C
C   OTHER SUBROUTINES REFERENCED BY HCVCP:
C      ESPAR - COMPUTATION OF EQUATION OF STATE PARAMETERS
C
C
      IMPLICIT REAL (A-H,O-Z)
      COMMON /ESPAR1/ AA,AB,BA,BB,F,C1,D1,C2,D2
      COMMON /REF/ TREFA,TREFB,HRA,HRB,SRA,SRB,VRA,VRB
      COMMON /HSPURE/ HPA,HPB,SPA,SPB,CP0A,CP0B
      COMMON /RDATA4/ R
      CALL ESPAR (IQ,T,X,A,B)
      B4=0.25*B
      VB=V+B
      VBL=LOG(V/VB)
      VB4=V-B4
      VB43=VB4**3
      RT=R*T
      IF (IQ.LE.3) THEN
C   COMPUTE MOLAR ENTHALPY AS A FUNCTION OF T, V, X
        H=X*(HPA-HRA)+(1.0-X)*(HPB-HRB)
     1    +((A+(A*D1/B-C1)*T)*VBL+A*(D1*T-B)/VB)/B
     1    +2.0*RT*V*(2.0*V-B4)*(B4-0.25*D1*T)/VB43
      END IF
      IF (IQ.GE.2) THEN
C   COMPUTE CONSTANT VOLUME MOLAR HEAT CAPACITY
        D12=D1*D1
        CV=X*(CP0A-R)+(1.0-X)*(CP0B-R)
     1    +(R*V*((0.375*D12*T/VB4+0.5*D2*T+D1)*(B4-2.0*V)
     1    +0.125*D12*T)/VB43
     1    +((1.0/VB+VBL/B)*(A*D2*B+2.0*(C1*D1*B-A*D12))/B
     1    -C2*VBL-A*D12/VB**2)/B)*T
        IF (IQ.EQ.3 .OR. IQ.EQ.5) THEN
C   COMPUTE MOLAR HEAT CAPACITY AT CONSTANT PRESSURE USING CV
          Y=B4/V
          DPDT=2.0*R/VB4*(-1.0+(-0.25*T*D1+(V*V*(1.0+0.75*T*D1/VB4))
     1      /VB4)/VB4)+(R+(-C1+A*D1/VB)/VB)/V
          DPDV=(-RT*(1.0+(4.0+(4.0+(-4.0+Y)*Y)*Y)*Y)/(1.0-Y)**4
     1      +A*(2.0*V+B)/VB**2)/V**2
          CP=CV-DPDT*DPDT*T/DPDV
        END IF
      END IF
      RETURN
      END
```

```
      BLOCK DATA BDESC
C
C   THIS ROUTINE INITIALIZES THE COMMON BLOCKS CONTAINING INFORMATION
C   ABOUT THE PURE COMPONENTS.  IT IS NOT REFERENCED DIRECTLY BY ANY
C   OTHER SUBROUTINE BUT MUST BE INCLUDED IN THE EXECUTABLE ELEMENT.
C   DATA ARRAYS ARE DIMENSIONED TO ACCOMODATE ADDITIONAL
C   PURE COMPONENTS.
C
C   EXPLANATION OF CONSTANTS:
C      COEFF(I,J) - FOR REFRIGERANT J, COEFFICIENTS OF A, B, CP0
C         CURVE FITS:
C         A = A0 * EXP(A1*T + A2*T*T)  (KJ M**3/KMOL**2)
C         B = B0 + B1*T + B2*T*T  (M**3/KMOL)
C         CP0 = C0 + C1*T + C2*T*T (KJ/KMOL K)
C         (STORED IN ORDER A0,A1,A2,B0,B1,B2,C0,C1,C2)
C      CRIT(I,J) - FOLLOWING INFORMATION FOR REFRIGERANT J:
C         I = 1 - MOLECULAR WEIGHT
C             2 - REFERENCE TEMPERATURE FOR ENTHALPY AND ENTROPY (K)
C             3 - CRITICAL TEMPERATURE (K)
C             4 - CRITICAL PRESSURE (KPA)
C             5 - CRITICAL VOLUME (M**3/KMOL)
C      HREF(J) - REFRIGERANT NAME (ASHRAE DESIGNATION)
C      HZERO(J) - VALUE OF SATURATED LIQUID ENTHALPY OF REFRIGERANT
C         J AT ITS REFERENCE TEMPERATURE (KJ/KMOL)
C      SZERO(J) - VALUE OF SATURATED LIQUID ENTROPY AT REFERENCE
C         TEMPERATURE (KJ/KMOL K)
C      R - GAS CONSTANT (KJ/KMOL K)
C      TOLR - RELATIVE CONVERGENCE TOLERANCE FOR ITERATION LOOPS
C         SHOULD BE AT LEAST 10 TIMES LARGER THAN MACHINE PRECISION
C      ITMAX - MAXIMUM ITERATION COUNT FOR ITERATIVE LOOPS
C      LUP - LOGICAL UNIT TO WHICH ANY WARNING MESSAGES ARE WRITTEN
C
      IMPLICIT REAL (A-H,O-Z)
      DIMENSION COEFF(9,20),CRIT(5,20),HZERO(20),SZERO(20)
      CHARACTER*6 HREF(20)
      COMMON /ESDATA/ COEFF,CRIT
      COMMON /HREF1/ HREF
      COMMON /HSZERO/ HZERO,SZERO
      COMMON /RDATA4/ R
      COMMON /TOL/ TOLR,ITMAX,LUP
      DATA R /8.314/
      DATA TOLR /1.0E-7/
      DATA ITMAX,LUP /20,6/
C
C   DATA FOR R11, R12, R13, R13B1, R14, R22, R23, R113, R114,
C   R142B, R152A FOLLOW.
C
C
C   R11, TRICHLOROFLUOROMETHANE
C
      DATA HREF(1) /'R11'/
      DATA (CRIT(I,1),I=1,5) /137.37,233.15,471.2,4467.,0.247/
      DATA HZERO(1),SZERO(1) /0.0,0.0/
      DATA (COEFF(I,1),I=1,9) /4971.54,-2.24669E-3,-5.11943E-7,
     1  0.176659,-1.74531E-4,-3.49717E-8,
     1  22.0418,0.260895,-2.45319E-4/
C
C  R12, DICHLORODIFLUOROMETHANE
C
      DATA HREF(2) /'R12'/
      DATA (CRIT(I,2),I=1,5) /120.91,233.15,384.95,4180.,0.217/
      DATA HZERO(2),SZERO(2) /0.0,0.0/
      DATA (COEFF(I,2),I=1,9) /3524.12,-2.77230E-3,-6.73180E-7,
     1  0.153755,-1.84195E-4,-5.03644E-8,
     1  17.5387,0.248546,-2.16271E-4/
C
C   R13, CHLOROTRIFLUOROMETHANE
C
      DATA HREF(3) /'R13'/
      DATA (CRIT(I,3),I=1,5) /104.46,233.15,302.0,3921.,0.181/
```

```
      DATA HZERO(3),SZERO(3) /0.0,0.0/
      DATA (COEFF(I,3),I=1,9) /2298.13,-3.41828E-3,-1.52430E-6,
     1  0.128141,-1.84474E-4,-1.07951E-7,
     1  13.9300,0.232181,-1.82929E-4/
C
C  R13B1, BROMOTRIFLUOROMETHANE
C
      DATA HREF(4)/'R13B1'/
      DATA (CRIT(I,4),I=1,5) /148.91,233.15,340.2,4017.,0.200/
      DATA HZERO(4),SZERO(4) /0.0,0.0/
      DATA (COEFF(I,4),I=1,9) /2728.10,-2.79791E-3,-1.50848E-6,
     1  0.139949,-1.82428E-4,-7.75898E-8,
     1  19.9537,0.216394,-1.70241E-4/
C
C   R14, TETRAFLUOROMETHANE
C
      DATA HREF(5) /'R14'/
      DATA (CRIT(I,5),I=1,5) /88.00,200.00,227.5,3795.,0.141/
      DATA HZERO(5),SZERO(5) /0.0,0.0/
      DATA (COEFF(I,5),I=1,9) /1393.60,-4.81985E-3,-1.89167E-6,
     1  0.100601,-1.94974E-4,-1.35408E-7,
     1  11.0629,0.209740,-1.40992E-4/
C
C   R22, CHLORODIFLUOROMETHANE
C
      DATA HREF(6) /'R22'/
      DATA (CRIT(I,6),I=1,5) /86.47,233.15,369.3,5054.,0.169/
      DATA HZERO(6),SZERO(6) /0.0,0.0/
      DATA (COEFF(I,6),I=1,9) /2514.59,-2.38706E-3,-1.83653E-6,
     1  0.113681,-1.16201E-4,-9.24562E-8,
     1  17.0547,0.161633,-9.12559E-5/
C
C   R23, TRIFLUOROMETHANE
C
      DATA HREF(7) /'R23'/
      DATA (CRIT(I,7),I=1,5) /70.01,233.15,299.1,4900.,0.133/
      DATA HZERO(7),SZERO(7) /0.0,0.0/
      DATA (COEFF(I,7),I=1,9) /2025.93,-4.68206E-3,9.95524E-7,
     1  0.103137,-2.29653E-4,1.55760E-7,
     1  20.4760,0.106183,-1.21892E-5/
C
C   R113, 1,1,2-TRICHLOROTRIFLUOROETHANE
C
      DATA HREF(8) /'R113'/
      DATA (CRIT(I,8),I=1,5) /187.38,233.15,487.5,3456.,0.329/
      DATA HZERO(8),SZERO(8) /0.0,0.0/
      DATA (COEFF(I,8),I=1,9) /7332.59,-2.20396E-3,-7.26656E-7,
     1  0.230713,-1.87956E-4,-1.06114E-7,
     1  76.2637,0.119641,7.18786E-5/
C
C   R114, 1,2-DICHLOROTETRAFLUOROETHANE
C
      DATA HREF(9) /'R114'/
      DATA (CRIT(I,9),I=1,5) /170.92,233.15,419.03,3304.,0.307/
      DATA HZERO(9),SZERO(9) /0.0,0.0/
      DATA (COEFF(I,9),I=1,9) /9771.35,-5.85557E-3,3.99413E-6,
     1  0.306318,-7.96444E-4,7.81059E-7,
     1  20.7005,0.464035,-4.17589E-4/
C
C   R142B, 1-CHLORO-1,1-DIFLUOROETHANE
C
      DATA HREF(10) /'R142B'/
      DATA (CRIT(I,10),I=1,5) /100.49,233.15,410.3,4120.,0.231/
      DATA HZERO(10),SZERO(10) /0.0,0.0/
      DATA (COEFF(I,10),I=1,9) /2990.00,-5.40563E-4,-4.12642E-6,
     1  0.146006,-8.92503E-5,-1.80562E-7,
     1  23.7611,0.231706,-1.06534E-4/
C
C   R152A, 1,1-DIFLUOROETHANE
C
```

```
      DATA HREF(11) /'R152A'/
      DATA (CRIT(I,11),I=1,5) /66.05,233.15,386.7,4492.,0.181/
      DATA HZERO(11),SZERO(11) /0.0,0.0/
      DATA (COEFF(I,11),I=1,9) /2254.37,-5.87778E-4,-4.37432E-6,
     1  0.116521,-9.04883E-5,-1.14563E-7,
     1  22.2804,0.154009,-3.06670E-6/
      END
```

```
      SUBROUTINE ESPAR (IQ,T,X,A,B)
C
C   THIS ROUTINE CALCULATES THE EQUATION OF STATE PARAMETERS AND THEIR
C   TEMPERATURE DEVIVATIVES AS A FUNCTION OF TEMPERATURE AND COMPOSITION
C   AS NEEDED BY THE OTHER PROPERTY ROUTINES.  BASED ON THE VALUE OF THE
C   INPUT QUALIFIER THE NECESSARY PARAMETERS ARE CALCULATED EXCEPT THAT
C   IF THE TEMPERATURE AND COMPOSITION ARE UNCHANGED FROM THE LAST CALL
C   THE PREVIOUS VALUES ARE USED.  THE TEMPERATURE DEPENDENCE OF THE
C   A, B, AND CP0 PARAMETERS ARE CONTAINED ENTIRELY WITHIN ESPAR AND
C   THE STATEMENT FUNCTIONS (IN BUBLT) FOR GIBBS FREE ENERGY
C   AND CHEMICAL POTENTIAL; ALTERNATE EXPRESSIONS FOR 'A' AND 'B'
C   REQUIRE CHANGING ONLY THESE ROUTINES.
C
C   INPUTS:
C      IQ - INPUT QUALIFIER
C         = 0 COMPUTE ONLY A AND B
C         >= 1 ALSO COMPUTE TEMPERATURE DERIVATIVES OF A AND B
C         >= 2 ALSO COMPUTE SECOND DERIVATIVE OF A AND B AND
C            IDEAL GAS HEAT CAPACITY
C         = 1, 2 OR 3 ALSO COMPUTE CONSTANTS FOR PURE COMPONENT ENTHALPY
C           AND ENTROPY
C      T - TEMPERATURE (K)
C      X - COMPOSITION (MOLE FRACTION COMPONENT A)
C
C   OUTPUTS:
C      A - 'A' PARAMETER FOR MIXTURE AT T, X
C      B - 'B' PARAMETER FOR MIXTURE AT T, X
C
C   OUTPUTS (VIA COMMON BLOCKS):
C      AA - 'A' PARAMETER FOR PURE COMPONENT A
C      AB - 'A' PARAMETER FOR PURE COMPONENT B
C      BA - 'B' PARAMETER FOR PURE COMPONENT A
C      BB - 'B' PARAMETER FOR PURE COMPONENT B
C      F - MIXTURE INTERACTION PARAMETER
C      DADT - TEMPERATURE DERIVATIVE OF A
C      DBDT - TEMPERATURE DERIVATIVE OF B
C      D2ADT2 - SECOND DERIVATIVE OF A WITH RESPECT TO TEMPERATURE
C      D2BDT2 - SECOND DERIVATIVE OF B WITH RESPECT TO TEMPERATURE
C      HPA - INTEGRAL OF CP0 WITH RESPECT TO TEMP FOR PURE A
C      HPB - INTEGRAL OF CP0 WITH RESPECT TO TEMP FOR PURE B
C      SPA - INTEGRAL OF (CP0 - R)/T WITH RESPECT TO TEMP FOR PURE A
C      SPB - INTEGRAL OF (CP0 - R)/T WITH RESPECT TO TEMP FOR PURE B
C      CP0A - PERFECT GAS HEAT CAPACITY FOR COMPONENT A (KJ/KMOL K)
C      CP0B - PERFECT GAS HEAT CAPACITY FOR COMPONENT B (KJ/KMOL K)
C
C
      IMPLICIT REAL (A-H,O-Z)
      COMMON /ESPAR1/ AA,AB,BA,BB,F,DADT,DBDT,D2ADT2,D2BDT2
      COMMON /RDATA1/ AA0,AA1,AA2,AB0,AB1,AB2,BA0,BA1,BA2,
     1  BB0,BB1,BB2,F0,F1
      COMMON /CPDATA/ CPA0,CPA1,CPA2,CPB0,CPB1,CPB2
      COMMON /HSPURE/ HPA,HPB,SPA,SPB,CP0A,CP0B
      COMMON /REF/ TREFA,TREFB,HRA,HRB,SRA,SRB,VRA,VRB
      COMMON /RDATA4/ R
      SAVE TLAST0,TLAST1,TLAST2,TLAST3,XLAST0,XLAST1,XLAST2,ALAST,
     1  BLAST,SQAB,XB,XB2,XBX,DAA,DAB,DBA,DBB,DSQAB,F0LAST,F1LAST
      DATA TLAST0,TLAST1,TLAST2,TLAST3,XLAST0,XLAST1,XLAST2 /7*-999./
      IF (IQ.LT.0) THEN
        IQ=ABS(IQ)
        GOTO 100
      END IF
      A=ALAST
      B=BLAST
      IF (T.NE.TLAST0) GOTO 100
      IF (F0.NE.F0LAST .OR. F1.NE.F1LAST) GOTO 110
      IF (X.NE.XLAST0) GOTO 120
      IF (IQ.LE.0) RETURN
      IF (T.NE.TLAST1 .OR. X.NE.XLAST1) GOTO 200
      IF (T.NE.TLAST3) GOTO 230
      IF (IQ.LE.1) RETURN
```

```
      IF (T.NE.TLAST2 .OR. X.NE.XLAST2) GOTO 300
      RETURN
  100 AA=AA0*EXP((AA1+AA2*T)*T)
      AB=AB0*EXP((AB1+AB2*T)*T)
      BA=BA0+(BA1+BA2*T)*T
      BB=BB0+(BB1+BB2*T)*T
      TLAST0=T
  110 F=F0+F1*T
      F0LAST=F0
      F1LAST=F1
      F=F0+F1*T
  120 X2=X*X
      XB=1.0-X
      XB2=XB*XB
      XBX=X*XB
      SQAB=SQRT(AA*AB)
      A=X2*AA+2.0*XBX*(1.0-F)*SQAB+XB2*AB
      B=X*BA+XB*BB
      ALAST=A
      BLAST=B
      XLAST0=X
      IF (IQ.LE.0) RETURN
  200 DAA=AA*(AA1+2.0*AA2*T)
      DAB=AB*(AB1+2.0*AB2*T)
      DBA=BA1+2.0*BA2*T
      DBB=BB1+2.0*BB2*T
      DSQAB=0.5*(AA*DAB+AB*DAA)/SQAB
      DADT=X2*DAA+XB2*DAB+2.0*XBX*((1.0-F)*DSQAB-F1*SQAB)
      DBDT=X*DBA+XB*DBB
      TLAST1=T
      XLAST1=X
  230 IF (IQ.LE.3) THEN
        HPA=(CPA0+(0.5*CPA1+CPA2/3.0*T)*T)*T
        HPB=(CPB0+(0.5*CPB1+CPB2/3.0*T)*T)*T
        SPA=(CPA0-R)*LOG(T/TREFA)+CPA1*(T-TREFA)+0.5*CPA2*
     1    (T*T-TREFA**2)
        SPB=(CPB0-R)*LOG(T/TREFB)+CPB1*(T-TREFB)+0.5*CPB2*
     1    (T*T-TREFB**2)
        TLAST3=T
      END IF
      IF (IQ.LE.1) RETURN
  300 D2AA=AA*((AA1+2.0*AA2*T)**2+2.0*AA2)
      D2AB=AB*((AB1+2.0*AB2*T)**2+2.0*AB2)
      D2SQAB=(0.5*(AA*D2AB+AB*D2AA)+DAA*DAB-DSQAB*DSQAB)/SQAB
      D2ADT2=X2*D2AA+XB2*D2AB+2.0*XBX*((1.0-F)*D2SQAB-2.0*F1*DSQAB)
      D2BDT2=2.0*(X*BA2+XB*BB2)
      CP0A=CPA0+(CPA1+CPA2*T)*T
      CP0B=CPB0+(CPB1+CPB2*T)*T
      TLAST2=T
      XLAST2=X
      RETURN
      END
```

```
      SUBROUTINE PLIMIT (T,A,B,VL,VU,PLOW,PUP)
C
C   GIVEN TEMPERATURE AND EQUATION OF STATE PARAMETERS, THIS
C   ROUTINE CALCULATES THE UPPER AND LOWER BOUNDS ON PRESSURE
C   FOR WHICH THERE ARE BOTH LIQUID AND VAPOR SOLUTIONS TO THE
C   EQUATION OF STATE.  IT CARRIES OUT TWO BISECTION METHOD
C   ITERATIONS TO FIND THE POINTS WHERE THE DERIVATIVE OF PRESSURE
C   W.R.T. VOLUME IS ZERO.
C
C   INPUTS:
C      T - TEMPERATURE (K)
C      A,B - EQUATION OF STATE PARAMETERS AT TEMPERATURE T
C
C   OUTPUTS:
C      PLOW - LOWER BOUND ON PRESSURE (PLOW CAN BE NEGATIVE, THE
C          CALLING PROGRAM MUST CHECK AND CORRECT FOR NEGATIVE
C          PRESSURES)
C      PUP - UPPER BOUND ON PRESSURE (KPA)
C      VL - MOLAR VOLUME AT PLOW (M**3/KMOL)
C      VU - MOLAR VOLUME AT PUP (M**3/KMOL)
C
C   OTHER SUBROUTINES REFERENCED:
C      NONE
C
C
      IMPLICIT REAL (A-H,O-Z)
      COMMON /RDATA4/ R
      COMMON /TOL/ TOLR,ITMAX,LUP
C
C   STATEMENT FUNCTIONS FOR THE EVALUATION OF PRESSURE AS A
C   FUNCTION OF V AND THE DERIVATIVE OF PRESSURE W.R.T
C   VOLUME AS A FUNCTION OF V
C
      P(RT,V,Y,A,B)=(RT*(1.0+(1.0+(1.0-Y)*Y)*Y)/(1.0-Y)**3
     1  -A/(V+B))/V
      DP(RT,V,A,B,B4,B42)=(-RT*(B42*B42+(-4.0*B42*B4+(4.0*B42
     1  +(4.0*B4+V)*V)*V)*V)/(V-B4)**4+A*(2.0*V+B)/(V+B)**2)/V**2
C
      B4=0.25*B
      B42=B4*B4
      RT=R*T
C
C   STARTING AT A VOLUME OF 12.0*B4 (WHICH HAS A POSITIVE SLOPE
C   FOR ALL 'REASONABLE' VALUES OF A, B, T) REDUCE THE VOLUME
C   UNTIL A NEGATIVE SLOPE OF P W.R.T. V IS FOUND AND THEN BEGIN
C   BISECTION METHOD TO FIND LOWER BOUND ON VOLUME AND PRESSURE.
C
      VC=12.0272727*B4
      V=VC
      DO 100 IT=1,ITMAX
      DPDV=DP(RT,V,A,B,B4,B42)
      IF (DPDV.LE.0.0) GOTO 116
      VPOS=V
      V=0.5*(V+B4)
  100 CONTINUE
  116 VNEG=V
      DO 120 IT=1,20
      VL=0.5*(VNEG+VPOS)
      DPDV=DP(RT,VL,A,B,B4,B42)
      IF (DPDV.LT.0.0) THEN
        VNEG=VL
      ELSE
        VPOS=VL
      END IF
  120 CONTINUE
      Y=B4/VL
      PLOW=P(RT,VL,Y,A,B)
C
C   STARTING AT V = 2*A/RT INCREASE V UNTIL A NEGATIVE
C   SLOPE IS FOUND; USE WITH V = 12.0*B TO BEGIN BISECTION
```

```
C   ITERATION FOR UPPER BOUND ON PRESSURE
C
      VPOS=VC
      V=2.0*A/RT
      DO 160 IT=1,ITMAX
      DPDV=DP(RT,V,A,B,B4,B42)
      IF (DPDV.LE.0.0) GOTO 164
      VPOS=V
      V=2.0*V
  160 CONTINUE
  164 VNEG=V
      DO 180 IT=1,20
      VU=0.5*(VNEG+VPOS)
      DPDV=DP(RT,VU,A,B,B4,B42)
      IF (DPDV.LT.0.0) THEN
        VNEG=VU
      ELSE
        VPOS=VU
      END IF
  180 CONTINUE
      Y=B4/VU
      PUP=P(RT,VU,Y,A,B)
      RETURN
      END
```

```
      SUBROUTINE VIT (T,P,A,B,VS,LLIQI,LVCON)
C
C   GIVEN TEMPERATURE, PRESSURE, AND EQUATION OF STATE
C   PARAMETERS, THIS ROUTINE CALCULATES THE LIQUID OR VAPOR
C   MOLAR VOLUME THAT SATISFIES THE EQUATION OF STATE.
C
C   INPUTS:
C      T - TEMPERATURE (K)
C      P - PRESSURE (KPA)
C      A,B - EQUATION OF STATE PARAMETERS AT TEMPERATURE T
C      VS - INITIAL GUESS FOR VOLUME.  IN ABSENCE OF BETTER
C         GUESSES SUGGESTED VALUES ARE:
C         LIQUID:  VS=0.8*B
C         VAPOR:   VS=R*T/P
C      LLIQI - LOGICAL VARIABLE
C         IF LLIQI = .TRUE. COMPUTE LIQUID VOLUME
C         IF LLIQI = .FALSE. COMPUTE VAPOR VOLUME
C      NOTE:  IF EITHER THE TEMPERATURE OR THE PRESSURE IS ABOVE
C         THE CRITICAL VALUE, ONLY ONE SOLUTION EXISTS AND THE
C         VALUE OF LLIQI HAS NO EFFECT.
C
C   OUTPUTS:
C      VS - MOLAR VOLUME (M**3/KG MOL)
C      LVCON - ERROR FLAG; IF LVCON = .TRUE. THE ITERATION HAS
C         NOT CONVERGED
C
C   OTHER SUBROUTINES REFERENCED:
C      NONE
C
C   (FOR EXPLANATION OF NOMENCLATURE SEE BUBLT)
C
C   NOTE:  THIS ROUTINE IS WRITTEN IN DOUBLE PRECISION EXCEPT
C      THAT THE ARGUMENTS ARE SINGLE PRECISION
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      LOGICAL LLIQ,LVCON,LLIQI
      REAL T,P,A,B,R,VS,TOLR,TC,PC
      COMMON /RDATA4/ R
      COMMON /TOL/ TOLR,ITMAX,LUP
      LVCON=.FALSE.
      LLIQ=LLIQI
      V=VS
      VL=LOG(V)
      PL=LOG(P)
      RT=R*T
      B4=0.25*B
      B4L=LOG(B4)
      IF (VL.LT.B4L) VL=B4L+0.5
      TC=A/(B*4.398909*R)
      PC=0.02386944*A/B**2
      VCL=LOG(12.0272727*B4)
      IF (P.GT.PC) THEN
        LLIQ=.TRUE.
      ELSE IF (T.GT.TC) THEN
        LLIQ=.FALSE.
      END IF
C
C   ENTER NEWTONS METHOD ITERATION FOR VOLUME.  FOR LIQUIDS
C   (OR FLUIDS ABOVE THE CRITICAL PRESSURE) THE ITERATION
C   IS CARRIED OUT IN TRANSFORMED COORDINATES OF LOG (V). FOR
C   VAPOR (OR FLUIDS AT SUPERCRITICAL TEMPERATURES BUT PRESSURES
C   BELOW THE CRITICAL VALUE) THE ITERATION IS IN TERMS OF
C   LOG (V) AND LOG (P).  THE ITERATION HAS CONVERGED WHEN
C   THE PRESSURE CALCULATED FROM THE EQUATION OF STATE AGREES
C   WITH THE INPUT PRESSURE.
C
      DO 100 IT=1,ITMAX
      IF (VL.GT.VCL .EQV. LLIQ) VL=VCL
      VLS=VL
      Y=B4/V
```

```
C
C   CALCULATE PRESSURE AS A FUNCTION OF VOLUME AND THE
C   DERIVATIVE OF THE PRESSURE W.R.T. LOG (VOLUME).
C
      P2=(RT*(1.0+(1.0+(1.0-Y)*Y)*Y)/(1.0-Y)**3-A/VB)/V
      DPDLV=RT/V*(-1.0+(-4.0+(-4.0+(4.0-Y)*Y)*Y)*Y)/(1.0-Y)**4
     1  +A*(2.0*V+B)/(V*VB*VB)
      IF (LLIQ) THEN
        IF (DPDLV.GE.0.0) THEN
          VL=0.5*(B4L+VLS)
        ELSE
          FVDP=(P2-P)/DPDLV
          IF (ABS(FVDP/P).LT.0.001*TOLR) THEN
            VS=EXP(VL-FVDP)
            RETURN
          ELSE
            VL=VL-FVDP
            IF (VL.LE.B4L) VL=0.5*(B4L+VLS)
          END IF
        END IF
      ELSE
        IF (DPDLV.GE.0.0 .OR. P2.LE.0.0) THEN
          VL=VL+0.5
        ELSE
          FVDPL=(LOG(P2)-PL)*P2/DPDLV
          IF (ABS(FVDPL).LT.0.001*TOLR) THEN
            VS=EXP(VL)
            RETURN
          END IF
          VL=VL-FVDPL
          IF (ABS(VL-VLS).GT.1.5) VL=VLS+SIGN(1.0D0,VL-VLS)
          IF (VL.LT.VCL) VL=0.5*(VLS+VCL)
        END IF
      END IF
      V=EXP(VL)
  100 CONTINUE
      LVCON=.TRUE.
      VS=V
      RETURN
      END
```

Example Run

The following example main program uses the property routines to calculate tables of saturation properties for a specified refrigerant mixture. Compiled versions of the following routines must be linked together before execution:

MAIN PROGRAM GRID

BCONST

BUBLT

ENTROP

HCVCP

BDESC

ESPAR

PLIMIT

VIT

The program reads the following information from data 'cards': (values used for the example are shown in parenthesis):

IR1, IR2 - code numbers for components of mixture (4,11)

F - mixture interaction parameter (0.0902)

TB, TE, TDELT - beginning and ending temperature and temperature interval for which to calculate properties (260., 340., 40.)

XB, XE, XDELT - beginning and ending composition and interval for which to calculate properties (0.0, 1.0, 0.1).

A listing of the main program and sample output follows.

```
      PROGRAM GRID
C   THIS PROGRAM SERVES TO TEST THE PROPERTY ROUTINES BY CALCULATING
C   TABLES OF DEW AND BUBBLE POINT PROPERTIES FOR A MIXTURE
C
C   INPUT INFORMATION:
C      IR1,IR2 - CODE NUMBERS FOR COMPONENTS OF MIXTURE
C      F0 - MIXTURE INTERACTION PARAMETER
C      TB,TE,DELT - BEGINNING & ENDING TEMPERATURE AND TEMPERATURE
C         INTERVAL FOR WHICH TO CALCULATE PROPERTIES
C      XB,XE,DELX - BEGINNING & ENDING COMPOSITION AND COMPOSITION
C         INTERVAL FOR WHICH TO CALCULATE PROPERTIES
C
C   OUTPUT INFORMATION (CALCULATED FOR EVEN INCREMENTS OF LIQUID
C      COMPOSITION)
C      XL - LIQUID COMPOSITION (MOLE FRACTION)
C      XV - VAPOR COMPOSITION (MOLE FRACTION) IN EQUILIBRIUM WITH XL
C      P - SATURATION PRESSURE (KPA)
C      VL - SATURATED LIQUID VOLUME (M**3/KMOL) AT COMPOSITION XL
C      VV - SATURATED VAPOR VOLUME (M**3/KMOL) AT COMPOSITION XV
C      HL - LIQUID ENTHALPY (KJ/KMOL) AT VL, XL
C      HV - VAPOR ENTHALPY (KJ/KMOL) AT VV, XV
C      SL - LIQUID ENTROPY (KJ/KMOL K) AT VL, XL
C      SV - VAPOR ENTROPY (KJ/KMOL K) AT VV, XV
C      CVL - CONST VOLUME HEAT CAPACITY (KJ/KMOL K) FOR LIQUID AT VL, XL
C      CVV - CONST VOLUME HEAT CAPACITY (KJ/KMOL K) FOR VAPOR AT VV, XV
C      CPL - CONST PRESSURE HEAT CAPACITY (KJ/KMOL K) FOR LIQUID
C      CPV - CONST PRESSURE HEAT CAPACITY (KJ/KMOL K) FOR VAPOR
C
C   OTHER SUBROUTINES REFERENCED:
C      ENTIRE SET OF PROPERTY ROUTINES EXCEPT FOR FITAB, FITF
C
      DIMENSION COEFF(9,20),CRIT(5,20)
      CHARACTER*6 HREF(20)
      LOGICAL LCRIT
      COMMON /ESDATA/ COEFF,CRIT
      COMMON /HREF1/ HREF
      COMMON /RDATA1/ A,B,F0,F1
      COMMON /TOL/ TOLR,ITMAX,LUP
      DIMENSION A(3,2),B(3,2)
      OPEN (UNIT=LUP,FILE='OUTPUT')
      READ (*,*) IR1,IR2,F0,TB,TE,DELT,XB,XE,DELX
      TC1=CRIT(3,IR1)
      TC2=CRIT(3,IR2)
      IF (TC1.GT.TC2) THEN
        I1=IR2
        I2=IR1
      ELSE
        I1=IR1
        I2=IR2
      END IF
      CALL BCONST (I1,I2,F0,0.0)
      DO 400 T=TB,TE,DELT
      WRITE (LUP,1000) T,HREF(I1),HREF(I2),F0
      DO 380 XL=XB,XE+TOLR,DELX
      CALL BUBLT (T,XL,XV,P,VL,VV,.TRUE.,LCRIT)
      IF (LCRIT) THEN
        LCRIT=.FALSE.
        WRITE (LUP,1040)
        GOTO 400
      END IF
      CALL HCVCP (3,T,VL,XL,HL,CVL,CPL)
      CALL HCVCP (3,T,VV,XV,HV,CVV,CPV)
      SL=ENTROP(T,VL,XL)
      SV=ENTROP(T,VV,XV)
      WRITE (LUP,1020) XL,XV,P,VL,VV
     1  ,HL,HV,SL,SV,CVL,CVV,CPL,CPV
  380 CONTINUE
  400 CONTINUE
      STOP
 1000 FORMAT ('1','DEW/BUBBLE LINES AT T =',F6.1,' K'/
```

```
     1  1X,'COMPONENT A: ',A6,'  COMPONENT B: ',A6/
     1  1X,'MIXING COEFFICIENT, F =',F7.4//
     1  1X,'      XL       XV       P       VL       VV'
     1  ,'       HL       HV       SL       SV       CVL      CVV',
     1  '      CPL      CPV'/
     1  1X,'      (MOL FRAC A)    (KPA)       (L/MOL)          ',
     1  '(KJ/KG MOL)       ',16('-'),' (KJ/KG MOL K) ',16('-'))
 1020 FORMAT (1X,2F9.4,F9.2,F9.5,F9.3,2F9.1,6F9.3)
 1040 FORMAT (/1X,'PSEUDO-PURE COMPONENT CRITICAL POINT EXCEEDED')
      END
```

DEW/BUBBLE LINES AT T = 260.0 K
COMPONENT A: R13B1 COMPONENT B: R152A
MIXING COEFFICIENT, F = .0902

XL	XV	P	VL	VV	HL	HV	SL	SV	CVL	CVV	CPL	CPV
(MOL FRAC A)		(KPA)	(L/MOL)		(KJ/KG MOL)		(KJ/KG MOL K)					
.0000	.0000	164.53	.06694	12.534	2142.6	22828.7	8.659	88.221	69.865	53.846	84.176	63.798
.1000	.4645	290.57	.06902	6.912	2688.9	20595.3	12.558	85.317	72.146	55.319	86.612	66.476
.2000	.6007	367.76	.07113	5.359	3117.8	19869.9	14.994	81.868	74.379	55.850	89.139	67.925
.3000	.6679	417.13	.07325	4.665	3434.9	19490.6	16.680	79.789	76.573	56.146	91.731	68.882
.4000	.7115	451.41	.07533	4.271	3645.0	19238.8	17.759	78.357	78.740	56.351	94.362	69.581
.5000	.7468	477.93	.07732	4.005	3751.8	19036.6	18.287	77.202	80.897	56.519	96.996	70.154
.6000	.7810	500.59	.07916	3.800	3758.5	18845.8	18.281	76.120	83.061	56.680	99.591	70.676
.7000	.8185	521.13	.08078	3.630	3667.7	18642.9	17.728	74.971	85.255	56.853	102.096	71.191
.8000	.8638	539.72	.08212	3.487	3481.4	18408.7	16.577	73.619	87.503	57.052	104.460	71.714
.9000	.9219	555.20	.08312	3.376	3201.5	18122.8	14.691	71.842	89.827	57.295	106.636	72.245
1.0000	1.0000	564.94	.08374	3.309	2830.3	17756.0	11.370	68.777	92.248	57.602	108.591	72.765

DEW/BUBBLE LINES AT T = 300.0 K
COMPONENT A: R13B1 COMPONENT B: R152A
MIXING COEFFICIENT, F = .0902

XL	XV	P	VL	VV	HL	HV	SL	SV	CVL	CVV	CPL	CPV
(MOL FRAC A)		(KPA)	(L/MOL)		(KJ/KG MOL)		(KJ/KG MOL K)					
.0000	.0000	633.54	.07384	3.459	5843.5	24746.6	21.753	84.764	80.305	60.335	101.599	74.688
.1000	.3166	889.39	.07655	2.372	6481.8	23074.0	25.944	84.140	81.698	61.336	103.842	78.331
.2000	.4628	1074.17	.07941	1.900	7007.7	22191.0	28.693	81.454	83.057	61.998	106.388	81.589
.3000	.5520	1211.95	.08238	1.639	7425.8	21603.4	30.710	79.282	84.387	62.502	109.222	84.510
.4000	.6175	1319.80	.08540	1.470	7739.6	21153.6	32.132	77.493	85.700	62.923	112.311	87.179
.5000	.6732	1408.84	.08837	1.350	7950.9	20770.1	33.008	75.907	87.018	63.304	115.578	89.697
.6000	.7263	1485.43	.09116	1.258	8060.2	20414.0	33.345	74.386	88.367	63.672	118.890	92.134
.7000	.7816	1552.17	.09364	1.185	8066.7	20062.5	33.118	72.816	89.783	64.044	122.034	94.495
.8000	.8429	1608.60	.09563	1.128	7968.5	19701.1	32.265	71.079	91.308	64.431	124.733	96.700
.9000	.9141	1651.65	.09697	1.088	7764.3	19318.9	30.637	68.977	92.984	64.836	126.697	98.566
1.0000	1.0000	1675.69	.09754	1.066	7454.0	18903.9	27.529	65.695	94.851	65.254	127.725	99.832

DEW/BUBBLE LINES AT T = 340.0 K
COMPONENT A: R13B1 COMPONENT B: R152A
MIXING COEFFICIENT, F = .0902

XL	XV	P	VL	VV	HL	HV	SL	SV	CVL	CVV	CPL	CPV
(MOL FRAC A)		(KPA)	(L/MOL)		(KJ/KG MOL)		(KJ/KG MOL K)					
.0000	.0000	1805.03	.08566	1.171	10408.8	25988.9	35.713	81.536	90.047	68.119	132.942	98.817
.1000	.2101	2220.09	.08994	.902	11139.1	24626.1	40.137	81.530	90.257	69.093	137.710	107.823
.2000	.3420	2555.91	.09475	.741	11775.6	23620.9	43.175	79.446	90.414	70.043	144.380	118.870
.3000	.4382	2833.51	.10016	.634	12324.2	22794.8	45.538	77.261	90.515	70.973	153.694	132.393
.4000	.5175	3069.21	.10617	.555	12789.0	22062.1	47.370	75.122	90.559	71.908	166.783	149.328
.5000	.5898	3274.10	.11275	.493	13170.9	21374.0	48.714	72.990	90.562	72.878	185.287	171.204
.6000	.6612	3453.69	.11971	.443	13464.6	20703.5	49.561	70.803	90.561	73.902	211.252	200.080
.7000	.7359	3607.84	.12658	.403	13654.8	20044.4	49.847	68.509	90.628	74.981	245.953	237.577
.8000	.8166	3731.12	.13246	.373	13712.4	19415.1	49.428	66.078	90.890	76.062	285.820	281.197
.9000	.9045	3814.41	.13606	.355	13598.6	18856.9	48.052	63.458	91.521	77.024	316.150	317.682
1.0000	1.0000	3847.56	.13629	.349	13284.5	18412.7	44.929	60.012	92.687	77.714	316.785	325.754

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This note describes the application of the Carnahan-Starling-DeSantis equation of state to halogenated hydrocarbon refrigerants and their mixtures. A complete and consistent set of thermodynamic functions is derived from the p-V-T equation of state and the perfect (ideal) gas heat capacities. A thorough discussion of reference states is included for both pure materials and their mixtures. Although this model exhibits a critical point, it does not quantitatively represent properties in the critical region. Despite this limitation, this model can represent both liquid and gaseous mixtures away from their own critical points, even at conditions near to and above the critical points of their components.

Algorithms and FORTRAN routines for the use of this model are presented along with the numerical coefficients for 11 pure refrigerants and 7 mixtures. Routines for evaluating the coefficients from saturation data are included. Several examples of the application of this equation of state are presented to demonstrate its versatility. The average deviation from the tabulated saturation properties of the 11 pure refrigerants is 0.54% for pressures, 0.09% for liquid volumes, and 0.50% for vapor volumes. It is shown to predict other properties of pure materials well and to describe the detailed features of mixtures, both phase diagrams and thermodynamic properties.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

equation of state; hard-sphere fluid; mixing rules; mixture; phase behavior; reference states; refrigerant; thermodynamic properties

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Gaithersburg, MD 20899

Official Business
Penalty for Private Use $300