Application of the Carnahan-Starling-DeSantis Equation of State to Mixtures of Refrigerants

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ABSTRACT

A modification to the Carnahan-Starling equation of state to describe the properties of refrigerant materials and their binary and ternary mixtures is discussed. A detailed discussion of the ability to fit and predict the thermodynamic properties of R22 is included. The representations arising from limited and extensive data sets are compared. The binary mixture R22/R114 is discussed and compared briefly to other binary refrigerant mixtures. The ability of this model to describe ternary mixtures without any ternary information is discussed. Present uses of this model are described.

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. 2a)
A	molar Helmholtz free energy
A_w	wall area
$b(b_{ij})$	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. 2b)
c_0, c_1, c_2	coefficients for the temperature dependence of C_p° (defined by Eqn 4)
C_p, (C_p°)	molar heat capacity at constant pressure (for the perfect gas state)
C_v	molar heat capacity at constant volume
E	internal energy
f(ij)	interaction parameter between species i and j
G	molar Gibbs free energy
H	molar enthalpy
MW	molecular weight
p	pressure
p∘	reference state pressure

p^*	pressure of perfect gas state at specified temperature and volume
$\dot{q}$	heat flow
R	gas constant
S	molar entropy
T, $(T_f$, $T_w)$	temperature (.of the fluid, .of the wall)
u_{sound}	speed of sound
V	molar volume
$x(x_i)$	molar composition (of species i)
y	b/4V
β	b/4
Γ	function defined by Eqns. 3 and 5
δ_{ij}	Kronecker delta function
μ_i	chemical potential of component i
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
ij	components i and j
ℓ, liq	liquid phase
sat	saturation conditions
v, vap	vapor phase

SUPERSCRIPTS

∘	perfect gas state
′	temperature derivative
″	second derivative with respect to temperature

INTRODUCTION

One of the most important tools in technical applications that involve phase equilibria -- separation in the chemical industry and working fluid properties in the thermal machinery industry -- is the ability to estimate the properties of the fluids accurately. Typically one cannot hope to have experimental

information for every possible condition encountered; thus, one must devise a scheme to use limited sets of data not only to estimate similar properties by interpolation but also to predict unmeasured properties. This paper describes such an approach for estimating the thermodynamic properties of pure refrigerant materials and their mixtures by using a fluid of hard spheres as a reference material.

The past decade has seen a surge of interest in the use of mixed refrigerant materials, fluorinated halomethanes and haloethanes, as working fluids in heat pump and power systems. Although the use of mixtures is not new, many of the important mixtures have been used near an azeotropic composition and have consequently been treated as pure materials. Mixtures where the components have a modest difference in volatility and do not form an azeotrope offer potential for increased efficiency and an expanded useful temperature range (1). The addition of new degrees of freedom in mixtures, the compositions, requires that one depart from the traditional and succesfully used scheme for describing the properties of pure materials, a set of often complex functions to describe separate properties -- vapor pressure, saturated liquid and vapor density, heats of vaporization, and other individual thermodynamic properties. By using a fluid mixture model, one can pull together all the thermodynamic properties of the mixture into a single, consistent scheme, and compensate for the dearth of information about the properties of the mixture.

In this paper, we describe the uses of an equation of state founded on a model that, in many ways, resembles the molecular features of the refrigerant materials, nearly spherical rigid objects with modest and only slightly directional intermolecular attractions. The equation of state is a modification of a form suggested by De Santis et al. (2): a hard-sphere term represented by the Carnahan-Starling equation (3) and an attractive term similar to the Redlich-Kwong attractive term (4).

THE EQUATION OF STATE AND PURE REFRIGERANT MATERIALS

The purpose of a practical equation of state is to represent the pressure, volume, temperature, and composition behavior of a material. When this function is combined with perfect gas heat capacities of the material, one can evaluate all its thermodynamic properties. It is inevitable that, regardless of the complexity of equation of state, it can only approximate the true behavior of a material, although a sophisticated function, such as the representation of the properties of water developed by Haar et al. (5), can represent properties within the uncertainty of their measurement over a huge range of conditions.

We have chosen to use an equation of state modeled on the properties of the hard sphere fluid in which there is a long range attraction. The form of the equation, suggested by De Santis et al. (2) consists of a hard-sphere, Carnahan-Starling (3), term, with an added Redlich-Kwong like (4) term. The choice of the Carnahan-Starling term over the two Percus-Yevick (6) representations of the hard-sphere fluid was arbitrary; at normal liquid densities, the three representations cannot be distinguished. The form of the equation of state is given in equation 1.

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

where $y = b/4V$.

In an exhaustive discussion of equations of state of this form, Henderson (7) has shown that an equation of state which contains the typical van der Waals, excluded volume term $RT/(V-b)$ is inevitably flawed; such an equation will require a complex attractive term to compensate for the shortcomings of the repulsive term. He further showed that a modified hard sphere equation of state could represent the properties of a fluid of small molecules well.

The pure fluid equation of state in this work contains six coefficients to represent the apparent temperature dependence of the effective hard-core diameter and the long-range attraction. The form of this temperature dependence is shown in equations 2a and 2b.

$$a = a_0 \exp(a_1 T + a_2 T^2) \qquad (2a)$$

$$b = b_0 + b_1 T + b_2 T^2 \qquad (2b)$$

These coefficients have been determined by evaluating "a" and "b" over a range of temperatures and by fitting them to the respective functions. The values of "a" and b were determined from the values of saturation liquid and vapor volumes and the equilibrium vapor pressures. Although these coefficients can be evaluated from the values of any thermodynamic property, their determination from the saturation properties, which are the most likely information to be available, is particularly straightforward. The three data at saturation are more than enough inormation to evaluate the quantities "a" and "b", which are uniquely related by the thermodynamic requirements that the pressures and the Gibbs free energies be equal in the two phases. The best value for these quantities was determined when the following function was minimized:

$$\Gamma(a,b,T) = \omega_\ell \left(\frac{V_{\ell,e} - V_{\ell,c}}{V_{\ell,e}} \right)^2 + \omega_v \left(\frac{V_{v,e} - V_{v,c}}{V_{v,e}} \right)^2$$
$$+ \omega_p \left(\frac{P_{sat,e} - P_{sat,c}}{P_{sat,e}} \right)^2 \qquad (3)$$

For calculating heat capacity and the temperature dependence of the enthalpy, entropy, and free energies, the heat capacities of the ideal gas states of the pure components are required. These are typically calculated from spectroscopic data and are in the literature for all the common refrigerants (8). In this work, C_p^o has been fit to a simple polynomial over the temperature range of interest:

$$C_p^o = c_0 + c_1 T + c_2 T^2 \qquad (4)$$

Table 1 gives all the thermodynamic functions that arise from this equation of state (9); Table 2 lists the quality of the fit for saturation properties with this equation of state for the more common refrigerants. With a few exceptions, the liquid volumes are fit to better than 0.1% and the vapor volumes and pressures are fit to better than 0.5% when compared to ASHRAE(10) tabulated values. The enthalpies of vaporization are predicted to about 1.0%; the enthalpy determination is a less severe test than it might seem; this quantity can be determined directly from the saturation data.

We have shown that this equation can be made to fit the saturation properties of these materials well.

Because large sets of non-saturation data do not exist in the public literature for many refrigerants, it is difficult to assess how well the equation of state reproduces these states. Extensive sets of data do exist For chlorodifluoromethane (R22); we shall use these data to explore the answers to three questions. How well can this equation of state predict other properties at saturation such as heat capacity? How well can the equation of state predict states far from saturation? Does including data in addition to saturation data substantially change the overall fit of the equation of state?

Figure 1 summarizes the ability of this equation of state to fit the saturation properties of R22. The saturation information used to produce the values of "a" and "b" was the correlation published in the ASHRAE tables of physical properties (10). Ideally, one would use actual data; for many of the refrigerants, however,

Table 1. The Thermodynamic Functions Arising from the Carnahan-Starling-DeSantis Equation of State

$$\frac{pV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V + b)} \quad ; \qquad y = b/4V$$

$$A(V, T) - A°(V, T) = - \frac{a}{b} \ln \left[\frac{V + b}{V}\right] + \frac{4RT\beta}{(V - \beta)} + \frac{RT\beta^2}{(V - \beta)^2} \quad ; \quad \beta = b/4$$

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

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

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

$$- \frac{ab_i}{b(V + b)} + \frac{2x_i a_i + 2x_j a_{ij}}{b} \ln \left[\frac{V}{V + b}\right]$$

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

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

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

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

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

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

$$C_p - C_v = - T \left[\frac{\partial p}{\partial T}\right]_{V,x}^2 \bigg/ \left[\frac{\partial p}{\partial V}\right]_{T,x}$$

$$u_{sound} = V \left[- \frac{C_p}{C_v} \frac{\partial P}{\partial V} \frac{1}{MW}\right]^{1/2}$$

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

TABLE 2. Comparison of ASHRAE (10) and Equation of State Values of Saturation Pressure, Saturated Liquid and Vapor Volumes and Enthalpy of Vaporization

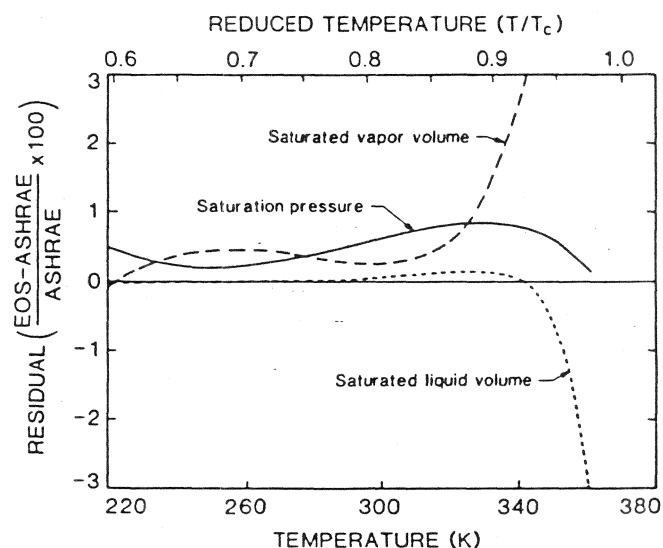| Refrigerant	% RMS Deviation			
	p(sat)	V(liq)	V(vap)	H(vap)-H(liq)
R11	0.41	0.04	0.45	0.87
R12	0.26	0.05	0.29	0.74
R13	0.10	0.02	0.14	0.17
R13B1	0.64	0.07	0.57	1.46
R14	0.18	0.01	0.18	0.35
R22	0.50	0.06	0.45	1.13
R113	0.22	0.03	0.23	0.61
R114	0.72	0.34	0.70	2.33
R142b	0.92	0.10	0.83	2.41
R152a	0.62	0.09	0.53	1.88
Average	0.54	0.09	0.50	1.35

Figure 1. Percentage difference between saturation pressures and saturated liquid and vapor volumes for R22 as tabulated by ASHRAE (10) and correlated by the equation of state.

one has access only to correlations. One can see that near the critical point, the quality of the correlation breaks down; this is characteristic of all the typically used equations of state. Efforts to fit the near critical features of a material without dramatically influencing the non-critical states near the critical temperature is not simple (11) and should not be tried without considerable thought.

Figure 2 summarizes the ability of the Carnahan-Starling-DeSantis equation of state to predict liquid and vapor isobaric molar heat capacities at saturation and the speed of sound in the saturated vapor. Unlike the enthalpy of vaporization, these quantities are not directly connected to the slope of the saturation line and the volume associated with vaporization. Since the evaluation of C_p involves taking a second temperature derivative of the Helmholtz free energy, it is a severe test of the hard sphere model. The deviations plotted in Figure 2 are with respect to the C_p correlation published by ASHRAE and
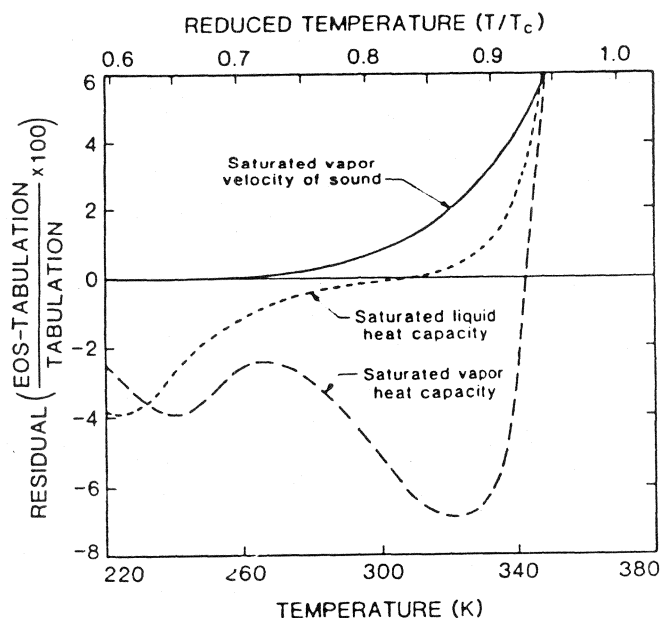

Figure 2. Percentage difference between saturated liquid and vapor isobaric heat capacities for R22 as tabulated by ASHRAE (10) and the speed of sound of the saturated vapor tabulated by JAR (12) and those respective properties predicted by the equation of state.

the speed of sound correlation published by the Japanese Association of Refrigeration (12). In all but the near-critical cases, where the isobaric heat capacity becomes large (and infinite near the critical point), the predicted value of the heat capacity agrees within a few percent of the correlated values. The deviation in the speed of sound increases steadily as the critical point is approached; not a surprising fact since the expression for u_{sound} (Table 1) involves C_p and the isothermal compressibility.

We have noted the existence of large sets of data on R22, much of it not saturation data. We shall now examine how well the equation of state produced only from saturation data can represent non-saturation data, how much of an improvement can be obtained by generating the equation of state parameters from all the data, and where the equation appears to break down in a serious way. Table 3 summarizes the deviations from different properties first by using only the equation of state generated from the ASHRAE correlation and then by using several extensive sets of data to evaluate "a" and "b" through a non-linear least squares routine from the IMSL

TABLE 3. Deviations of Calculated Property from Experimental Property for Chlorodifluoromethane (R22) for Coefficients Based on Saturation Data Alone and for Coefficients Based on the Total Data Set.

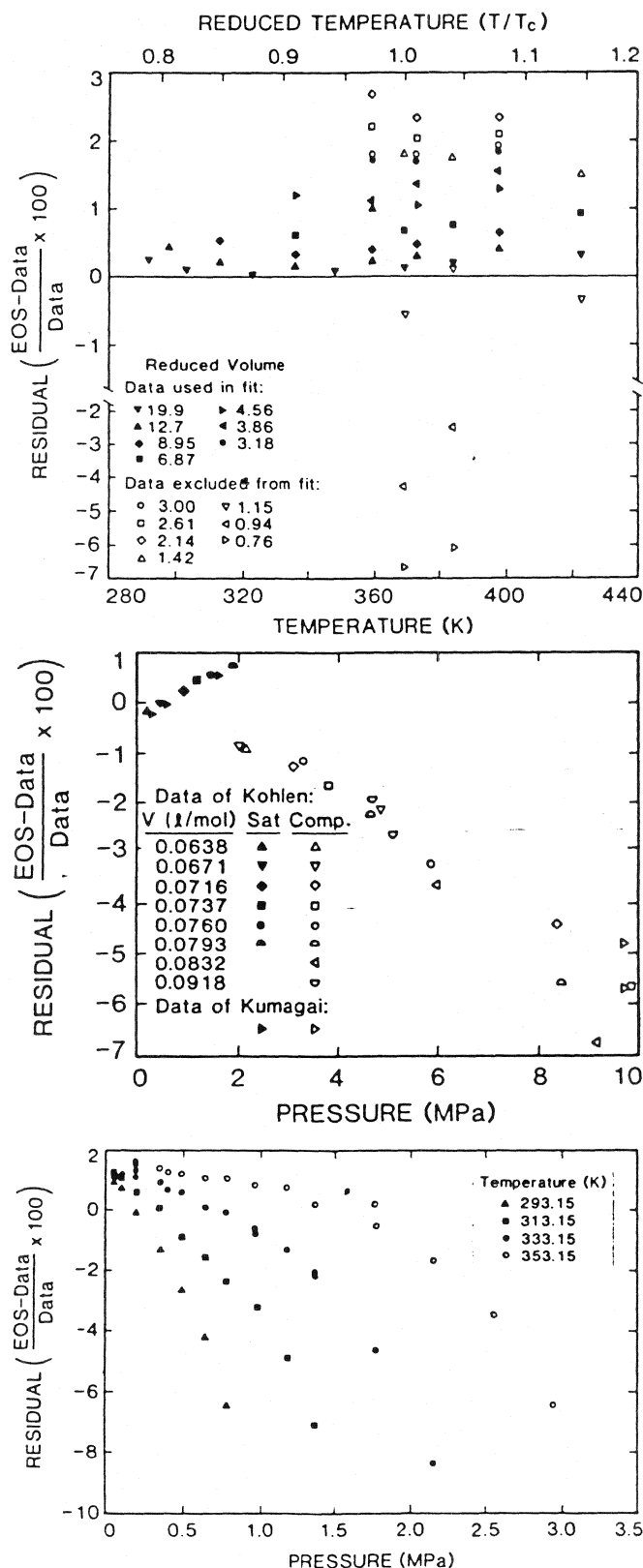| Property	Wt. of Data Set	%RMS (sat. only)	%RMS (total set)
P(sat)(28,29)	75	0.69	0.20
V(liq,sat)(29,30)	60	0.089	0.39
V(liq,P,T)(29,30)	1.7	4.15	3.71
V(vap,P,T)(31)	67	1.39	1.07
H(vap)-H(liq)(32)	1.5	0.64	0.92
C_p(liq)(32)	0.2	2.66	3.40
C_p(vap)(14,13)	3.3	2.80	2.91

Figure 3. Deviations between the measured and calculated properties for R22: (a) pressure of the superheated vapor as a fuction of temperature and reduced volume (31); (b) saturated and compressed liquid volumes (29, 30); isobaric heat capacities of the superheated vapor (13, 14).

Statistical Library available on the NBS central computing facility. The weighting of different data sets was determined by the size of the set and the uncertainty of the quantity involved. The most striking result represented in this table is that the quality of the fit is only slightly changed; although the overall fit of the entire data set is somewhat improved.

The details of the deviation between the property predicted by the equation of state and the measured property are shown for comparison in Figures 3a-c. Although the fit is generally quite good, there are several regions where the quality of the fit is poor: the critical region and the highly compressed, high temperature liquid states, where the error in the volumes exceeds a few percent. We have noted before that this equation of state, as well as the commonly used industrial equations of state, will not behave properly in the near-critical region. In the highly compressed liquid states, the volume is underpredicted. Real molecules are, of course, not rigid spheres and, evidently, the effective hard sphere volumes which best fit the saturated liquid and superheated vapor data is too small. Thus at high pressures and temperatures, the equation of state mimics a fluid with too soft a central core. However at pressures where refrigerants are normally used (less than 2.5 MPa) this departure from the actual behavior of the fluid is not strongly manifested; liquid volumes are thus typically fit to within 1%. The isochoric heat capacities in the superheated vapor region are seen to be consistently underpredicted (Fig. 7c) except at pressures approaching zero where the equation of state overpredicts C_p by about 1.5%. The C_p expression derived from the equation of state was analytically and numerically confirmed to approach the ideal gas value in the limit of zero pressure. However, the data of Ernst et al. (13) and Bier et al. (14), upon extrapolation to zero pressure are not in agreement with the theoretical values of C_p^o presented in the JANAF Tables, upon which the values of C_p^o in the equation of state were based.

There are two lessons that can be drawn from this exercise. First, the saturation information alone gives a good indication of the overall ability of the equation of state to represent even the non-saturation fluid properties of a material. Second, except for states where the equation of state is known to be poor -- the critical region and highly compressed fluid states -- the equation of state can be extended well into the single-phase fluid regions with a precision similar to that indicated by the saturated fit alone.

BINARY MIXTURES

The equation of state can be modified to describe mixtures by allowing the parameter "a" and "b" to be functions of the composition. We have used the normal Lorentz-Berthelot mixing rules (15) to relate the values of "a" and "b" of the mixture to the values for the pure components; the value of "a" is further modified by the addition of an empirical parameter, the interaction parameter f(12):

$$a = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} \qquad (5a)$$

$$\text{where } a_{12} = (1-f(12)) (a_{11}a_{22})^{1/2}$$

$$b = x_1 b_1 + x_2 b_2 \qquad (5b)$$

There are many empirical and semiempirical ways of estimating the values of f(12) (16, 17). It may often

be possible to estimate its value successfully; however, many of these schemes collapse for no apparent reason. The values for f(12) for a variety of refrigerant mixtures are given in Table 4. All these values have been determined from experimental dew and bubble information on the mixture. When dew or bubble curve information is known, f(12) has a value that minimizes the following function:

$$\Gamma(T, x_\ell, f(12)) = \omega_p \left[\frac{P_{sat,e} - P_{sat,c}}{P_{sat,e}} \right]^2 + \omega_\ell \left[\frac{v_{\ell,e} - v_{\ell,c}}{v_{\ell,e}} \right]^2$$

$$+ \omega_v \left[\frac{v_{v,e} - v_{v,c}}{v_{v,e}} \right]^2 + \omega_x (x_{v,e} - x_{v,c})^2 \qquad (6)$$

There are few refrigerant mixtures for which there are extensive data. The mixture R22 plus dichlorodifluoromethane (R12) was once used commercially; it contains an azeotrope over part of its temperature range. Morrison and McLinden (18) have shown that, by using the normal boiling temperatures for this mixture (19), the model could predict the temperature dependence of the azeotropic composition. Measurements for the mixture bromotrifluoromethane (R13B1) plus 1,1-difluoroethane (R152a) (18) have been used to evaluate f(12); this information to has then been used to model heat pumps (20) and evaluate heat transer coefficients (21).

TABLE 4. Values of f(12), the Mixing Parameter for Selected Refrigerant Mixtures

Mixture	f(12)	deviation	type of data
R13B1/R152	0.089	0.004	bubble point(18)
R22/R12	0.041	0.009	normal boiling point(19)
R23/R13	0.089	0.010	bubble point(33)
R13/R12	0.035	0.010	bubble point(34)
R12/R152a	0.035	0.004	azeotrope composition(35)
R22/R114	0.03	0.02	bubble point(22)
R23/R12	0.088	0.020	bubble point(36)
R11/R22	0.037	0.008	bubble point(37)
R12/R114	0.000	0.002	bubble point(38)
R11/R12	0.005	0.012	bubble point(39)
R22/R13B1	0.025	0.011	bubble point(40)

A third mixture for which there are extensive data (22) is R22 plus 1,2 dichlorotetrafluoroethane (R114). These extensive data indicate the possibility of a composition dependence of f(12). This behavior is shown in Figure 4. Care should be taken, however, in interpreting such a result. The large deviations near the extremes of the composition range could result from systematic errors when data for the mixtures and the pure components arise from different data sets. Small inconsistencies near the pure component axes will give rise to large uncertainties in f(12). The error bars in Fig. 4 shown the uncertainty associated with a 0.5% uncertainty in the pressure; the data clearly indicate a variation outside this range. Study of the systems reported in Table 4 suggests a strong correlation between the composition variation of f(12) and the relative volatility of the components in the mixture; f(12) is lower for compositions rich in the more volatile component in nearly all the cases examined. The behavior may relect a flaw in the mixing rule; large differences in volatility are typically associated with large differences in molecular size. The mixing rule for the molecular size coefficient (Eqn. 5b) becomes progressively more inaccurate as the size difference increases.

We have noted in the preceding section that one cannot expect a quantitative representation of the near critical region. There are, however, certain situations where the existence of a critical point and the ability of the proper hard-sphere kernal to represent the liquid state of the fluid can be used to an advantage. Morrison (23) has pointed out many of the van der Waals-like equations of state, e.g. Redlich-Kwong and Redlich-Kwong-Soave, are designed only for use in the vapor phase and that some other scheme must be used to estimate the properties of the liquid phase. Whenever all the components in a mixture are far from their respective critical points and each has an "ordinary" liquid phase, a variety of interpolation schemes can be used effectively. Whenever this condition is not met, such an approach will collapse.
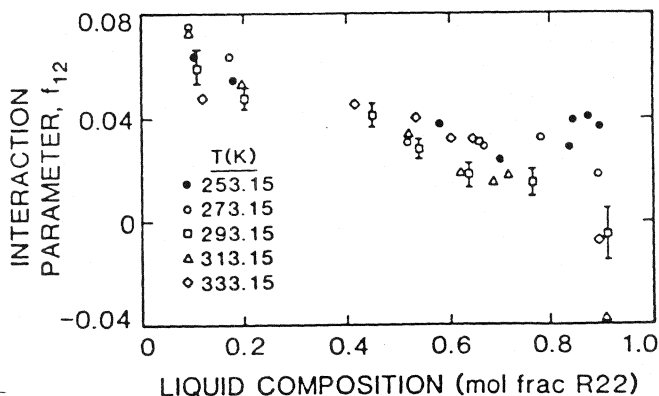

Figure 4. Variation of the mixture interaction parameter, f(12), with temperature an composition for the mixture R22/R114 using the data of Hackstein (22); error in f(12) due to experimental uncertainty indicated for the values at 293 K.

The possibility of encountering critical temperatures in refrigerants is not a mere academic point. Although the critical temperature of many refrigerant materials is well above the upper range where they are used, that is not universally true. For example, any mixture containing trifuoromethane (R23) above T = 26°C would be affected. Even if the critical point of the mixture is well outside the range of operation, an equation of state, not an interpolation of liquid properties, would be necessary to estimate the liquid properties of such a mixture.

MIXTURES WITH THREE OR MORE COMPONENTS

In the previous section, the equation of state was modified to describe binary mixtures. The model can be expanded to include any number of components by making "a" and "b" functions of the entire composition of the mixture. In the binary mixture model, the composition dependence of these parameters was limited to simple pair interactions; there were no terms higher than second order in the composition dependence. If this kind of model is adequate for more complex mixtures, one need know only the binary interaction pairs. Using this approximation, the form for the two molecular parameters becomes the following:

$$b = \sum_i x_i b_i \qquad (7a)$$

6

$$a = \left[\sum_i x_i a_{ii}^{1/2}\right]^2$$

$$- \left[\sum_i \sum_j f(ij) \, x_i x_j (1 - \delta_{ij}) a_{ii}^{1/2} a_{jj}^{1/2}\right] \qquad (7b)$$

Measurements of the bubble point conditions for the ternary mixture R22 plus R12 plus R114 were measured using an apparatus that has been described by Morrison and Kincaid ([24]). The measured bubble point pressures and liquid phase molar volumes and the corresponding calculated properties are given in Table 5. The calculated pressures agree, on average, with the measured pressures to within 1% at all three temperatures; the uncertainty in the experimental pressures is +/- 0.0002 MPa for pressures below 15.0 MPa and +/- 0.0003 MPa for pressures higher than 15.0 MPa. The calculated molar volumes also agree with the measured volumes within 1%; the experimental uncertainty in the volumes is +/- 0.5%. One should note that this mixture is not ideal. The mixture R12/R22 has an azeotrope over part of this temperature range. As was discussed in the previous section, the vapor pressure for R22/R114 has a strong positive deviation from Raoult's law. Only the mixture R12/R114 is nearly ideal.

These data suggest that, for mixtures of refrigerants where one does not encounter strong, almost chemical interactions -- such as hydrogen bonding -- a model constructed on only pair interactions can reproduce the properties of mixtures within a percent of their actual values. This conclusion suggests that one needn't make measurements on mixtures of three or more components; thus, the properties of complex mixtures are accessible once the properties of all the binary pairs are known. A similar useful conclusion was discussed by Wright ([25]) is his application of the Redlich-Kwong-Soave equation of state to the vapor phase of ternary refrigerant mixtures.

APPLICATIONS

In the earlier sections of this paper, we have explored the extent to which a simple representation of a hard sphere fluid with a long range intermolecular attraction can be used to describe refrigerants and their mixtures. In this section, we shall briefly describe the application of this model to two research applications. The first application was the use of the thermodynamic program as part of a two phase flow experiment to determine heat transfer coefficients. The second was as part of a computer model of a heat pump charged with a non-azeotropic refrigerant mixture. In both applications, a Padé approximant ([26]) was used to describe the phase boundary in order to speed up the computations.

In an extensive set of experiments performed by Ross ([21]), both the individual components and mixtures for the system, R13B1 plus R152a were run through a 2.7 m long, 9 mm diameter stainless steel tube. The tube was heated by passing a DC current along its length. At various points along the tube the wall temperature, T_w, was measured; by knowing the voltage drop and current, one could evaluate the total energy supplied to the test section, and, thus, the change in the enthalpy with respect to the inlet conditions. Given the overall mass flow rate and the pressure, temperature, and composition of the fluid as it was introduced into the test section, one could, by means of the equation of state algorithms,

TABLE 5. Predicted and Experimental Bubble Properties for the Mixture R114/R12/R22

X(R114)	X(R12)	T(K)	P(MPa) (exp.)	(pred)	V(liq)(l/mol) (exp.)	(pred)
0.654	0.072	283.083	0.3464	0.3444	0.1021	0.1034
		308.047	0.6782	0.6756	0.1077	0.1090
		333.027	1.1916	1.1916	0.1154	0.1173
0.587	0.086	283.083	0.3870	0.3815	0.1005	0.1010
		308.047	0.7509	0.7449	0.1065	0.1068
		333.027	1.3114	1.3109	0.1136	0.1153

calculate the quality and equilibrium vapor temperature T_f, at each test point. The heat transfer coefficient, α, evaluated by the following relation, was studied for a variety of system conditions:

$$\alpha = \frac{\dot{q}}{A_w(T_w - T_f)} \qquad (7)$$

A second application of the modified hard sphere model is as part of Domanski's ([20]) computer simulation of a heat pump system charged with a non-azeotropic refrigerant mixture. The heat pump system has four fundamental parts, a compressor, a condensor, an expansion device, and an evaporator. In this model, both heat exchangers are composed of banks of tubes that not only interact with the air flowing past them but also with one another because of their proximity and relative position to one another in the air flow. Domanski's simulation then calculates the change of enthalpy in every part of the exchanger; the mixture model described earlier in this paper provides both the phase states and the thermodynamic information of the fluid. The heat pump simulation coupled with the fluid model then allows one to examine the effectiveness of a mixture as a working fluid under a variety of both ambient and machinery operating conditions.

In both these applications, the users took advantage of the accuracy and the relative algebraic simplicity of the model. Ross found that when he set his experiment up so that all the refrigerant was evaporated, the calculated temperature change in the experimental rig and the measured change agreed within 1 K of one another.

CONCLUDING REMARKS

In this brief review, we have explored the application of the Carnahan-Starling-DeSantis equation of state to refrigerant materials and their mixtures. From a theoretical perspective, the one advantage of this model is that it can be used for the liquid state, something not generally true for van der Waals-like equations of state. We have shown that, when the molecular parameters in the equation of state are generated from the saturation data alone, the equation of state fits broad areas of the one-phase properties with nearly the same degree of fit. We have further shown that binary mixtures of refrigerants can be readily described by a simple modification of this equation; however, the evaluation of the appropriate mixture parameters must be determined experimentally. Once the binary mixture parameters are known, the properties of mixtures with more components can be

predicted accurately. Finally, we have cited two examples in which the thermodynamic algorithms associated with this model have been linked to a machinery simulation package in one case and a two-phase fluid flow experiment in the other. Both applications benefitted from the algebraic simplicity of the model and its numerical accuracy.

The ability of this equation of state to correlate the saturation properties of refrigerants vary from material to material. The quality of the fit appears to be strongly dependent upon polarity and molecular complexity. Nonetheless, this is a six parameter equation of state; for those materials where it best represents both the liquid and vapor properties, it is as good a representation as correlation schemes using more that four times as many parameters. Because of the fundamental character of the physical foundation of the model, compensation both for charge distribution and small departure from sphericity can be made readily (27) and should be the next step in the development of this model.

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