

The Importance of Including the Liquid Phase in Equations of State for Nonazeotropic Refrigerant Mixtures

G. Morrison, Ph.D.

ABSTRACT

The recent surge of interest in nonazeotropic refrigerant mixtures has generated a need for correlation and prediction of liquid phase information for mixtures. We show that the ideal mixture assumption (the linear weighting of pure liquid properties) can be useful but can also be seriously in error when one of the components is near its critical point, even when the mixture is not near its own critical point. We also suggest that using spline-fits to data in isolation is an ineffective way of using such information. A physical model is suggested for a mixture whose equation of state incorporates all the departures of the mixture from ideality, which allows small, isolated sets of data to be used in predicting other physical properties of both the pure fluids and their mixtures.

INTRODUCTION

An equation of state may be viewed on at least two levels. First, it may be thought of as a way of correlating and storing an immense amount of experimental information, in particular, the relation among density, pressure, and temperature and also composition in the case of mixtures. Second, it may be viewed as the fundamental relationship between all the thermodynamic properties of a material, which, when derived from a physical model, can be connected to the molecular character of that material.

A good example of how an equation of state has evolved from the former to the latter view is the virial equation of state for gases. In 1885, Thiesen proposed an equation of the form

$$\frac{PV}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \dots \quad (1)$$

to describe the behavior of gases.

Kammerlingh-Onnes (1901) showed that such an equation described the p-v-T properties of many gases well. It was he who named the coefficients the virial coefficients from the Latin word for force. By 1937, J. G. Mayer was able to show how this expression arose naturally from a statistical mechanical model. He was also able to connect the experimental values of the virial coefficients to the molecular properties of the fluid.

The application of practical equations of state to liquids and dense fluids is undergoing such an evolution. The properties of such materials are dominated by the short-range, essentially hard-body repulsion between the molecules. Two approaches to the problem of describing dense fluids are the following: to use a spline function that fits existing experimental information or to construct elaborate corrections to the van der Waals equation of state,

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad (2)$$

*Graham Morrison is in the Thermophysics Division of the Center for Chemical Engineering at the National Bureau of Standards.

THIS PREPRINT FOR DISCUSSION PURPOSES ONLY. FOR INCLUSION IN ASHRAE TRANSACTIONS 1985, V. 91, Pt. 1. Not to be reprinted in whole or in part without written permission of the American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., 1791 Tullie Circle, NE, Atlanta, GA 30329. Opinions, findings, conclusions, or recommendations expressed in this paper are those of the author(s) and do not necessarily reflect the views of ASHRAE.

In a review of the van der Waals class of equations, such as the Redlich-Kwong-Soave (1972) equation, Henderson (1979) has shown that such expressions are fundamentally flawed at high densities because the packing problem has not been properly addressed.

Mixing of species is a further complication in fluids. We shall show that the linear combination of spline fits to pure liquid properties for predicting liquid mixture properties has a limited useful range and that such a technique can lead to a serious misrepresentation of the mixture. It is thereby important that dense fluids, both of pure and mixed species, be represented well by an equation of state. Considering Henderson's previously noted conclusions and taking a lesson from the example of the virial equation of state, one should use an equation of state in which the treatment of the liquid phase is firmly founded on a physical model.

The limitations of the linear combination scheme for predicting the properties of mixtures is discussed below with specific examples. An equation of state that uses a hard sphere fluid as a reference is introduced and its ability to produce other thermodynamic information from a relatively small set of input information is discussed by comparing experimental and predicted thermodynamic properties for the refrigerant R152a.

THE IDEAL MIXTURE APPROXIMATION

Depending upon the demands placed on liquid-phase information, mixture properties can be guessed in a variety of ways. The simplest guess can be made by a mole fraction (or mass fraction) average of the molar (or specific) properties of the pure components. For example, to guess the molar volume of a mixture such as R13B1/R152a, one would use the following relation:

$$v(x) = x_{R13B1} v_{R13B1} + x_{R152a} v_{R152a} \quad (3)$$

The quantities v_{R13B1} and v_{R152a} should be the molar volumes of the two pure components in the same phase state and at the same temperature and pressure as the mixture. When only saturated liquid volumes are known and where this guessing scheme is satisfactory, the use of saturated liquid data causes no important change in the quality of the guess. The quantities x_{R13B1} and x_{R152a} are the respective mole fraction of the two components. Mixtures described by such relations are called ideal mixtures. Large departures from equation 3 can result when there are strong directional interactions between the components of the mixture--hydrogen bonding or even a chemical reaction--and where the components themselves will separate if the temperature is slightly changed. For example, in a mixture of ethanol and water that is 55.1 mole percent water, this simple predictive scheme is in error by $-1.08 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ (-3.0%) (Marsh and Richards 1980). Typically, the fluorinated hydrocarbons and halocarbons being considered for nonazeotropic refrigerant mixtures do not fall into this class. For a mixture where an interaction such as hydrogen bonding is not important (e.g., carbon tetrachloride and benzene), equation 3 is off by a few hundredths of a percent in molar volume (Bottomley and Scott 1974).

It would appear that guessing the properties of liquid phases by such a linear combination scheme is both straightforward and adequate--but not perfect. This simple approach suffers from two major flaws. The first, and most obvious, involves thermodynamic consistency. There is no guarantee that independent spline fits through often unrelated measurements of different thermodynamic quantities will be consistent with one another. Because a spline fit contains quite restricted information along a special path, there is often no way to derive other thermodynamic quantities from it. For example, the temperature derivation of the saturated liquid specific enthalpy does not produce a specific heat at constant pressure (Rowlinson and Swinton 1982a), although when far from the critical point, the difference may be small. The second flaw occurs at conditions when one of the components is near its critical point. Here the linear scheme breaks down completely. This effect will be discussed in the next section.

CRITICAL POINTS AND LIQUID MIXTURES

Typically, the chemical process industry has avoided operating near a critical point. Pressures are usually high (>40 bar), and the advantages inherent in having two distinct phases are lost. For similar reasons, such conditions should be avoided in heat pumps. Nonetheless, critical phenomena can dramatically affect simple predictive schemes such as the one described in the previous section.

Suppose we were operating with a 50/50 mole percent mixture of R13B1/R152a at 158 F (70°C). At that temperature, the mixture has perfectly well-behaved liquid and vapor phases and, for the mixture, the critical point is not a problem. The temperature is above the critical point of R13B1 (at 67°C) so that there is no liquid state information for R13B1 to put into equation 3. Obviously, equation 3 does not apply when conditions are above the critical point of at least one of the components. The difficulty with the linear combination scheme does not begin at the critical point, however. As the temperature approaches 67°C from below, the specific volume of R13B1 along the saturation line expands dramatically until, at the critical point, the liquid and gas specific volumes are identical. The specific volume of a material at its critical point is roughly three times its volume as a normal liquid. Similar rapid changes occur in all the specific properties of a material near its critical point, enthalpy, entropy, and heat capacity at constant pressure, to name a few. Thus, in a binary mixture where the mixture and one of its components are normal liquids and the other component is near to, but below, its critical temperature, the molar properties predicted by expressions similar to equation 3 can be in error by as much as 50%-100%. Wormald et al. (1979a, 1977b) have measured the onset of the critical point effect in departures from linear combinations like equation 3 in the enthalpy and in the volume. For the mixtures argon/nitrogen (1977a) and argon/methane (1977b), the effect of the critical point of the argon on the mixture could be observed 20K below the critical point. Wormald (1977c) has examined these effects by using several equations of state and found that any equation of state that has a critical point can describe the effect at least qualitatively and that some equations of state can reproduce the effect quantitatively. Although a mixture such as R13B1/R152a may appear to have little in common with Ar/CH₄ and Ar/N₂, one would expect the same kind of effects because their phase diagrams have much in common. Because phase diagrams scale roughly in proportion to the critical properties, one would expect to detect similar effects as much as 40K below the critical point of R13B1, that is, even at room temperature!

Figure 1 shows how such errors can arise. In this illustration, which plots molar volume against mole fraction, the temperature is near to, but still 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. Below ab in the figure are the low-volume, hence, liquid and higher pressure, states of the mixture. The curve af is the isobar having 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. Were one to use the prescription described by equation 3, one would draw a straight line between a and b or, more correctly, a and f. In both cases, the straight line and the curves deviate by about 15% from one another in the mid-composition range. Of course, by the nature of the prescription, the curve and the line must coincide at pure A and B.

We can conclude the following about linear combination schemes for treating the properties of liquid mixtures:

1. Far from the critical point of either component, they are likely to give satisfactory estimates of the mixture properties, so long as there are no strong directional interactions in the liquids and so long as the liquid components are not likely to separate.
2. Spline-fits for liquids typically give a one-dimensional description of a property along a special path, so that thermodynamic consistency with other properties and calculation of other properties through thermodynamic relations are difficult to check.
3. Even when the mixture itself is not near its critical point, the linear combination scheme of predicting the properties of liquid mixtures breaks down when one of the components is within 30-40K of its critical point.
4. Departure from ideal liquid mixture behavior (behavior predicted by the linear combination scheme) can be dealt with by proper equations of state.

AN EQUATION OF STATE

During the past quarter century, there has been a major research effort to describe dense fluids quantitatively with a minimum number of arbitrary constraints on the model. With the development of fast, large computers, much has been learned about two kinds of fluids, one composed of hard spheres (Barker and Henderson 1955; Carnahan and Starling 1969) and the other

composed of molecules that attract one another at moderate and large distances and repel one another at short distances. The best known of this latter group is the Lennard-Jones fluid (Verlet and Levesque 1967). Indeed, so much is known about these theoretical materials that they can be used as references against which all dense fluid behavior can be compared. The most important feature is not that these model fluids describe a particular fluid exactly but that they contain the proper treatment of the high density states. Recalling the virial equation of state, one would expect that equations of state founded on such models would retain a simplicity not necessarily found in an arbitrary function chosen to fit the data and, in addition, would retain a physical meaning to its parameters.

One such fluid is a mixture of hard spheres with a weak, long-range attraction. The Carnahan-Starling (1969) equation will be used to describe the hard-sphere reference fluid:

$$\left(\frac{pv}{RT}\right)_{HS} = \frac{1 + y + y^2 - y^3}{(1 - y)^3}; \quad y = b/4v \quad (4)$$

The attractive perturbation appears as a variation on the Redlich Kwong attractive term to yield the following equation:

$$\left(\frac{pv}{RT}\right) = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(v + b)} \quad (5)$$

This particular form was suggested by DeSantis et al (1976); however, similar forms of the perturbed hard sphere equation have been used by Mansoori and Leland (1972) and Wormald (1977c), to name a few.

In this model, b , related to the hard sphere diameter, and a , the measure of the intermolecular attraction, are allowed to be temperature dependent. Although the temperature dependence is an empirical device, it does have a physical justification. Real molecules are not hard spheres; as the temperature rises, they approach one another more closely. The term, b , is a measure of this closest approach and becomes smaller as T increases. Few real molecules are spherically symmetric; as the temperature rises, important directional interactions tend to be "washed out" by increased rotation; hence, the term a also decreases with increasing T . One way of modeling a mixture is the "one fluid" model, which treats the single-phase mixture as if it were a single component fluid with some averaged intermolecular properties (Rowlinson and Swinton 1982b). The parameters a and b are made composition-dependent by using the so-called Lorentz mixing rules (1981) as follows:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

where

$$a_{ij} = (a_{ii} a_{jj})^{1/2} (1 - f_{ij} (1 - \delta_{ij})) \quad (7)$$

where

δ_{ij} is the Kronecker delta function, and

$$b = \sum_i x_i b_i \quad (8)$$

The function, f_{ij} , empirically accounts for interactions of unlike species that would not be expected from like molecular interactions. Gubbins and Twu (1978) have invested considerable effort to understand the origin of f_{ij} and evaluate it from a molecular model.

Let us briefly consider how the value of a and b are determined for R152a. In this description, we see an example of how an isolated set of information and a good physical model can not only correlate isolated data well but also predict other physical properties of the material. The input information for evaluating a and b are the saturated liquid and vapor molar volumes and the equilibrium vapor pressure in the temperature range where the equation will be used. The values of a and b that minimize the value of the following relation were determined by a simple linear regression scheme:

$$f = \left(\frac{v_l - v_l'}{v_l} \right)^2 + \left(\frac{v_g - v_g'}{v_g} \right)^2 + \left(\frac{p - p'}{p} \right)^2 \quad (9)$$

In this expression, the primed quantities are those determined by the equation of state; the unprimed quantities, input information. The values of a and b at different temperatures were then fit to quadratic polynomials in temperature. The p - v - T equation of state, such as the one in equation 4, can be used to evaluate all the thermodynamic properties associated with the phase transition. Functions consistent with equation 4 are shown in Table 1.

TABLE I. THERMODYNAMIC FUNCTIONS ARISING FROM THE PERTURBED CARNAHAN-STARLING EQUATION OF STATE

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

$$y = b/4v$$

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

$$\beta = b/4$$

$$G(p^*, T, v) = GPB(p^*, T) + RT \ln \frac{RT}{p^*v} - \frac{a}{b} \ln\left(\frac{v + b}{v}\right) + \frac{2RT\beta}{(v - \beta)^3} (4v^2 - 4v\beta - \beta^2) - \frac{a}{v + b} - \frac{RT\beta}{(v - \beta)^2}$$

$$\mu(p^*, T, x_i, v) = G(p^*, T, x_i, v) + (1 - x_i) \left(\frac{\partial G}{\partial x_i} \right)_{T, p} = \mu PB(p^*, T, x_i) + RT \ln \frac{RT}{p^*v} + \frac{RT\beta(4v - 3\beta)}{(v - \beta)^2}$$

$$+ \frac{RT\beta_i(4v^2 - 2v\beta)}{(v - \beta)^3} + \frac{ab_i}{b^2} \ln\left(\frac{v + b}{v}\right)$$

$$- \frac{ab}{b(v + b)} + \frac{2x_i a_i}{b} \ln\left(\frac{v}{v + b}\right)$$

$$S(v, T, x) = SPB(v, T, x) + \frac{a'b - ab'}{b^2} \ln\left(\frac{v + b}{v}\right) + \frac{ab'}{v(v + b)}$$

$$- \frac{R\beta(4v^2 - 3\beta)}{(v - \beta)^2} - \frac{RT\beta'(4v^2 - 2v\beta)}{(v - \beta)^3}$$

$$E(v, T) = EPB(v, T) + \frac{a'bT - ab'T - ab}{b^2} \ln\left(\frac{v + b}{v}\right)$$

$$+ \frac{ab'T}{b(v + b)} - \frac{RT^2\beta'(4v - 2v\beta)}{(v - \beta)^3}$$

$$H(p, T, v) = HPB(T) + \frac{a'bT - ab'T - ab}{b^2} \ln\left(\frac{v + b}{v}\right)$$

$$+ \frac{ab'T - ab}{b(v + b)} + \frac{RT(4v - 2v\beta)(\beta - \beta'T)}{(v - \beta)^3}$$

$$\begin{aligned}
C_v(v,T) = & C_v^P(T) + \frac{6RT^2\beta'^2(v\beta - 2v^2)}{(v - \beta)^4} \\
& + \frac{2RTv((\beta''T + 2\beta')(\beta - 2v) + \beta^2T)}{(v - \beta)^3} \\
& - \frac{Tab'}{b(v + b)^2} + \frac{T(ab''b + 2a'b'b + 2ab'^2)}{b^2(v + b)} \\
& - \frac{(a''b^2T - 2a'b'bT + 2ab'^2T - ab''bT)}{b^3} \ln\left(\frac{v + b}{v}\right) \\
C_p = C_v - T & \left(\frac{\partial p}{\partial T}\right)_{v,x}^2 / \left(\frac{\partial p}{\partial v}\right)_{T,x}
\end{aligned}$$

Figure 2 shows the correlation of the liquid and vapor saturated volumes and the vapor pressures. Figure 3 shows the correlation of the enthalpy of vaporization. The correlated properties, which agree with published values to a few tenths of a percent, are well within the experimental uncertainties of the properties of R152a (Mears et al. 1955).

The p-v-T equation of state is not sufficient to determine the temperature dependence of quantities such as the enthalpy, the entropy, or the total heat capacity. The equation of state has been integrated over the volume to produce the Helmholtz free energy function, from which all other thermodynamic functions arise. Associated with that integration is a constant dependent on temperature alone that can be evaluated by knowing the perfect gas heat capacity for each of the components in the mixture. Fortunately, the perfect gas properties are known for R152a (Chen et al. 1975); such data typically arise from spectroscopic information rather than calorimetric measurements.

We have now produced a scheme for generating the thermodynamic properties of a material such as R152a. That scheme results from the wedding of a modest set of isolated experimental information--the saturated liquid and vapor densities and the vapor pressure--a theoretical model with a firm physical foundation--the perturbed hard-sphere model--and the perfect gas information. Although further experimental information could have been included in this scheme, we have chosen not to do so for the following reasons: first, for many fluids, the liquid-vapor saturation data are the only reliable information available; second, data sets from different laboratories and of different thermodynamic properties are often inconsistent with one another for instrumental reasons. Unless differences between data sets are well understood, mixing them does not necessarily improve the fit of a model (Haar and Gallagher 1984).

To test this scheme, let us compare the value of C_p for the saturated liquid state of R152a calculated from the equation of state, a measured value for C_p (Radermacher 1983) the values of C_p appearing in the ASHRAE tables (ASHRAE 1977), and an experimental base data correlation published by the National Engineering Laboratory (NEL 1981) in the United Kingdom. A comparison of these four sets of information is shown in Figure 4. The four sets agree well at the high-temperature end of the range; however, at the low-temperature end, the ASHRAE information is consistently low. The most striking feature of Figure 4 is that C_p has been evaluated without reference to any previously measured liquid heat capacities and, yet, it compares well with the experimental information. Such agreement indicates the virtue of the perturbed hard sphere model, since the heat capacity involves the evaluation of a second derivative of the free energy, a strong test for physical consistency. The ASHRAE table values, which do not agree with measured values of C_p nearly so well, indicate the shortcomings of data correlation schemes that have been in common use in the past.

Before considering the properties of the mixture, it is essential to understand the status of mixture models. The most accurate models exist for mixtures where the components are chemically similar and there are no major directional forces between the molecules, as, for example, in mixtures of hydrocarbons. The major approximation in nearly all mixture models is that properties peculiar to the mixture can be inferred from the properties of the pure

components. As the components become more dissimilar either in size or in chemical nature, this approximation becomes ever less satisfactory in representing the mixture. Typically, an empirical correction is made to compensate for departures of the model from the true properties of the mixture. Such a correction, which can be determined only by doing experiments on the mixture, appears as the function f_{ij} in equation 6. In the model proposed here, data for the mixture R13B1/R152a (Morrison and Neal n.d.)--bubble pressures and saturated liquid volumes and compositions--have been used to calculate the value of f_{ij} and its temperature dependence. The equation of state parameters for R13B1 were determined in the same way as for R152a.

Figure 5a shows the vapor pressure fit of experimental data by the equation of state; figure 5b shows the molar volume. One should note that the experimental temperature is only 12K from the critical point of pure R13B1. The equation of state reproduces the expected curvature of the $v_{sat} - x$ line, a feature that could never be handled by the linear weighting scheme. Figure 6 shows the calculated behavior of C_p at this same temperature. The value of C_p , which becomes infinite near the critical point of a pure fluid, varies dramatically over the composition range, from the near critical R13B1 to the "normal" R152a. The equation of state reproduces the expected behavior. In this case, a linear weighting scheme would be in error by 25% for the 50/50 mixture. One should note that for this example a 50/50 mixture itself is not near a critical point; nonetheless, the critical point of one of the reference fluids strongly influences the predicted properties of the mixture when an "ideal" mixing scheme is used. There will be large errors in predicting volumes and enthalpies; however, the ideal mixing scheme collapses completely in predicting thermodynamics response functions such as heat capacity and compressibility.

CONCLUSIONS

An equation of state for fluids derived from a realistic physical model has a number of advantages. First, it has the potential for analytic simplicity as well as a legitimate physical interpretation of the parameters in the equation. Second, such an equation is able to describe mixtures not only where the departures from ideal mixing are small but also in situations where the ideal mixing scheme is doomed to failure when one of the components is near its critical point, even when the mixture itself is not near a critical point.

Further an equation of state that uses the hard sphere fluid as a reference can correlate isolated data sets and use them to produce a universal description of the material, even when those sets of information are very restricted. Such an equation of state can withstand the test of being differentiated at least twice in being able to predict values of C_p within the uncertainty of the experimental measurements. Finally, even when such an equation is fit to mixture data, it retains both the simplicity and palpable physical interpretation of the pure fluids.

NOMENCLATURE

- a (a_{ij}) = the equation of state parameter associated with intermolecular attraction (between species i and j)
- a' (a'') = the first (and second) derivative of a with respect to temperature
- A (APB) = the molar Helmholtz free energy (of a perfect gas reference fluid)
- b (b_i) = the equation of state parameter associated with the hard core of a molecule (of species i)
- b' = the temperature derivative of b
- B = the second virial coefficient
- C = the third virial coefficient
- C_v (C_p) = the molar heat capacity at constant volume (pressure)
- E (EPB) = the molar internal energy (of a perfect gas reference fluid)
- f = a function defined by equation 8

f_{ij}	= an empirical function to compensate for the real behavior in a mixture of species i and j
G (G ^{PS})	= the molar Gibbs free energy (of a perfect gas reference fluid)
H (H ^{PS})	= the molar enthalpy (of a perfect gas reference fluid)
p	= the pressure
p^*	= the pressure of a perfect gas reference fluid equal to the saturation pressure of the pure component at the temperature T
R	= the gas constant
S (S ^{PS})	= the molar entropy (of a perfect gas reference fluid)
T	= the thermodynamic temperature
v	= the molar volume
x_i	= the mole fraction of component i
y	= a function defined in equation 4
β	= $b/4$
β_i	= $b_i/4$
β'	= $b'/4$
δ_{ij}	= the Kronecker delta
μ_i	= the chemical potential of species i

REFERENCES

- ASHRAE. 1977. "Thermodynamic properties of refrigerants." New York: American Society of Heating, Refrigerating and Air Conditioning Engineers, Inc.
- Barker, J. A. and Henderson, D. 1971. Mol. Phys. 21, p. 787; Reiss, H., 1955. Adv. Chem. Phys. 8, p. 1.
- Bottomley, G. A. and Scott, R. L. 1974. J. Chem. Thermodynamics, 6, p. 973.
- Carnahan, N. F. and Starling, K. E. 1969. J. Chem. Phys., 51, p. 635.
- Cartwright, G. 1981. NEL Report No. D(PP)SR5. East Kilbride, United Kingdom, National Engineering Laboratory.
- Chen, S. S.; Rodgers, S. A.; Chao, J.; Wilhoit, R. C., and Zwolinski, B. J. 1975. J. Phys. Chem. Ref. Data, 4, p. 441.
- De Santis, R.; Gironi, F., and Marrelli, L. 1976. Ind. Eng. Chem., Fundam., 15, p. 183.
- Gubbins, K. G., and Twu, C. H. 1978. Chem. Eng. Sci., 33, p. 863; 33, p. 879.
- Haar, L. and Gallagher, J. S. 1984. "Estimate of the accuracy for the HGK Helmholtz function," Report to IAPS (International Association for the Properties of Steam, Dr. Howard J. White, Jr., Secretary, National Bureau of Standards, Gaithersburg, Maryland 20899), 31 January.
- Henderson, D. 1979. "Equations of state in engineering and research," K. C. Chao and R. L. Robinson, Jr., editors, Advances in Chemistry, vol. 182, p. 1, Washington, American Chemical Society.

- Kammerlingh Onnes, H. 1901. Comm. Phys. Chem. Lab. Leiden, Nos. 71 and 74.
- Lorentz, H. A. 1881. Amr. Phys., 12, p. 127.
- Mansoori, A. and Leland, T. W., Jr. 1972. Faraday Transactions II, 68, p. 320.
- Marsh, K. N. and Richards, A. E. 1980. Aust. J. Chem., 33, p. 2121.
- Mayer, J. G. 1937. J. Chem. Phys., 5, p. 67.
- Mears, W. H.; Stahl, R. F.; Orteo, S. R.; Shair, R. C.; Kells, L. F.; Thompson, W., and McCann, H. 1955. Ind. and Eng. Chem., 47, p. 1449.
- Morrison, G. and Neal, T. B. to be published.
- Radermacher, R. 1983. Private communications.
- Rowlinson, J. S. and Swinton, F. L. 1982a. "Liquids and liquid mixtures", London, Butterworth Scientific, p. 15. 1982b. *ibid.* Chapter 8.
- Soave, G. 1972. Chem. Eng. Sci., 27, p. 1197.
- Verlet, L. and Levesque, D. 1967. Physica, 36, p. 254.
- Watson, J. T. R. 1981. NEL Report No. D(PP)SR4, East Kilbride, United Kingdom, National Engineering Laboratory.
- Wormold, C. J.; Lewis, K. L., and Mosedale, S. E. 1977a. J. Chem. Thermodynamics, 9, p. 221; Mosedale, S. E. and Wormold, C. J. 1977b. J. Chem. Thermodynamics, 9, p. 483, Wormold, C. J. 1977c. J. Chem. Thermodynamics, 9, p. 643.

ACKNOWLEDGMENTS

This work was supported in part by the Electric Power Research Institute. The author also wishes to thank L. Haar, R. Radermacher, D. Didion, and P. Domanski for their assistance and comments.

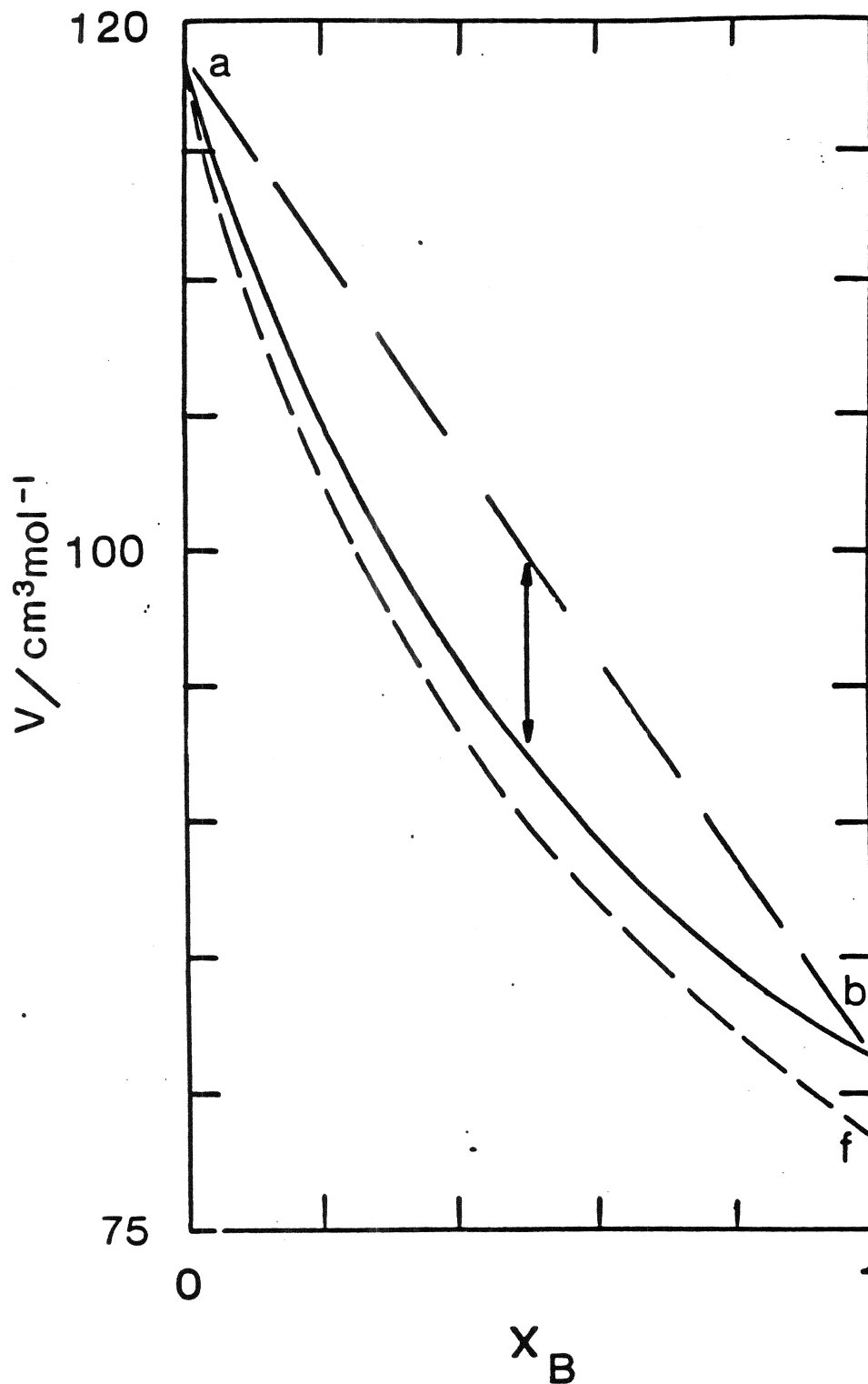


Figure 1. The behavior of the liquid phase of a representative mixture A/B at a constant temperature. The temperature is approximately 97% the critical temperature of A and 83% the critical temperature of B. The solid curve, ab, is the locus of volumes at the saturation conditions for the mixture; the broken line, ab, represents the prediction of the saturation volume using a linear combination estimate. The double-headed arrow indicates the error between the estimated and the actual saturation volumes. The curve, af, is the locus of mixture volumes at constant pressure, the saturation pressure of pure A

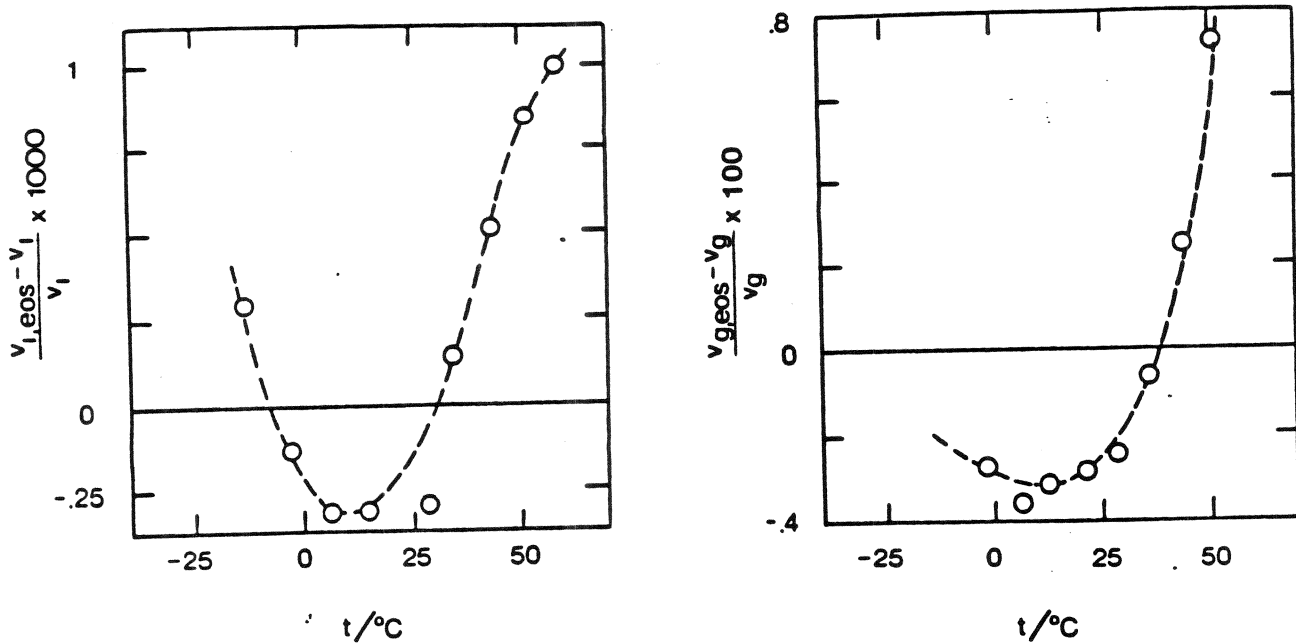
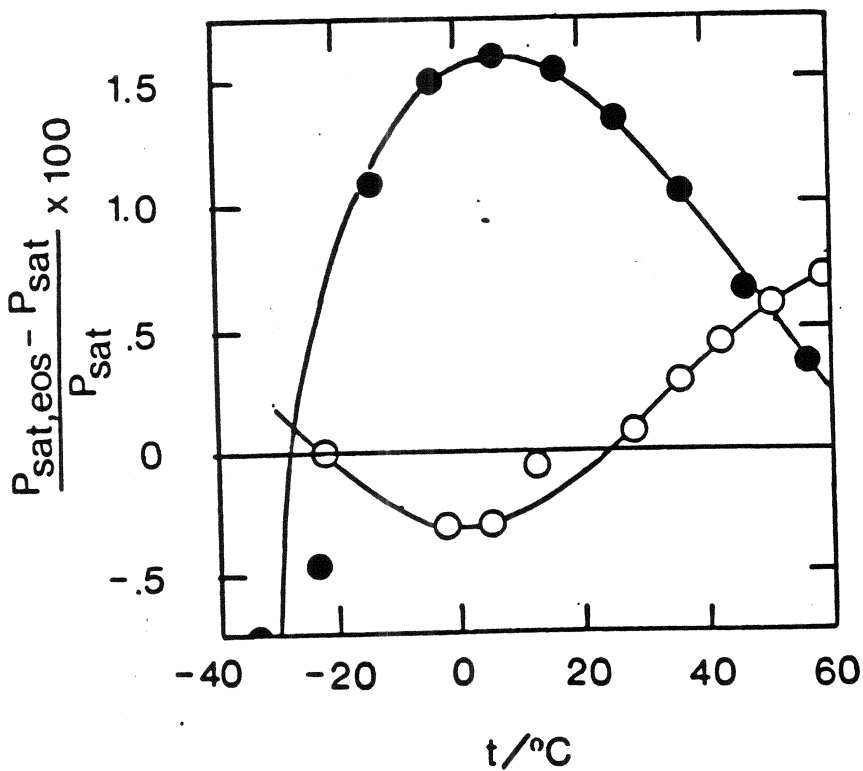


Figure 2. A comparison between the saturation properties of R152a as predicted by the equation of state and tabulated values of those properties. In all cases, the open circles refer to the MELPAC (Watson 1981, Cartwright 1981) tabulation: (a) liquid saturation volumes, (b) vapor saturation volumes, and (c) vapor pressures (the filled circles refer to data from the ASHRAE (1977) tabulation)



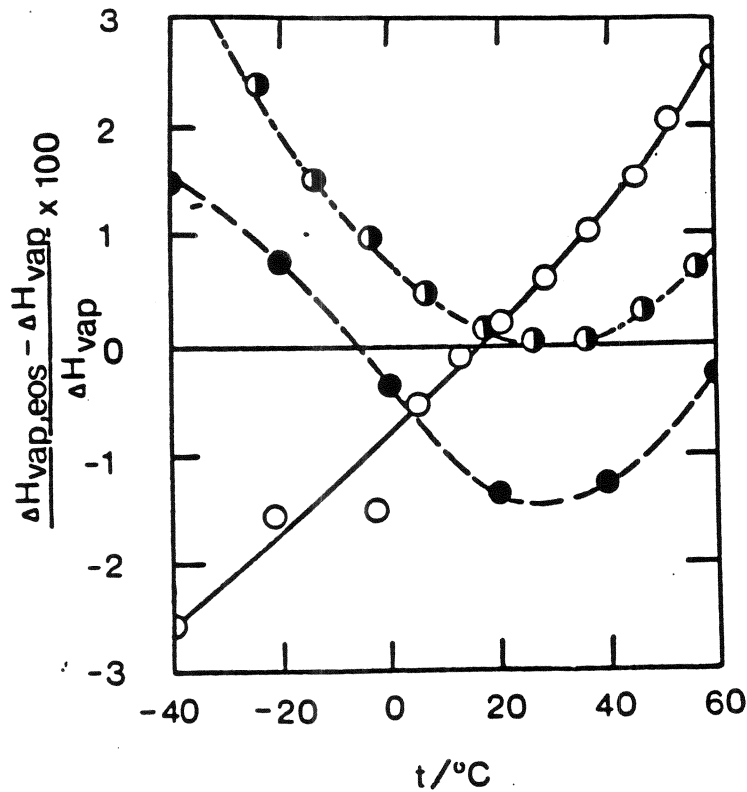


Figure 3. A comparison of the enthalpy of vaporization for R152a predicted from the equation of state and tabulated values of that property. The open circles refer to the NELPAC (Watson 1981, Cartwright 1981) tabulation, the half-filled circles to the ASHRAE (1977) tabulation, and the filled circles to data published by Mears et al. (1955). The enthalpy of vaporization is a derived rather than a correlated property

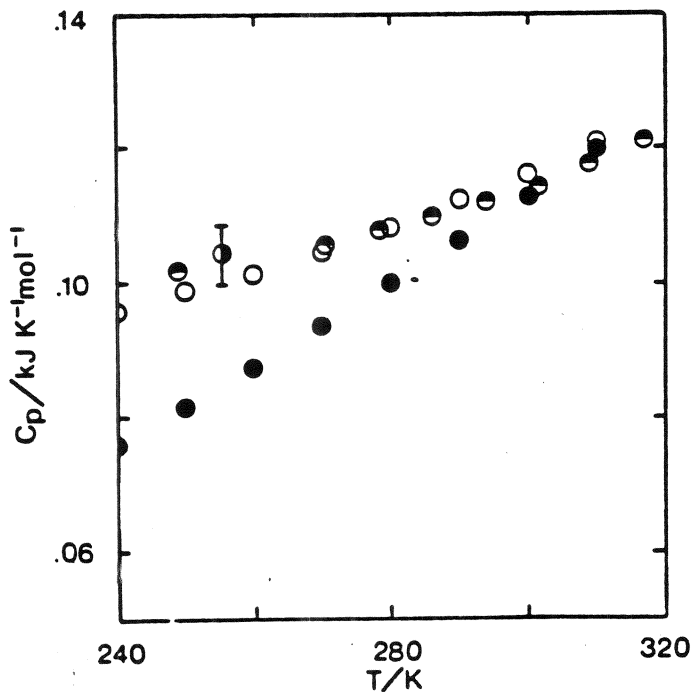


Figure 4. The molar heat capacity at constant pressure along the liquid branch of the saturation line for R152a. The filled circles refer to the ASHRAE (1977) tabulation; the upper half-filled circles refer to the NELPAC (Watson 1981, Cartwright 1981) tabulation; the right half-filled circle refers to a single measurement made by Rademacher (1983), the open circles refer to the values predicted by the equation of state (this work)

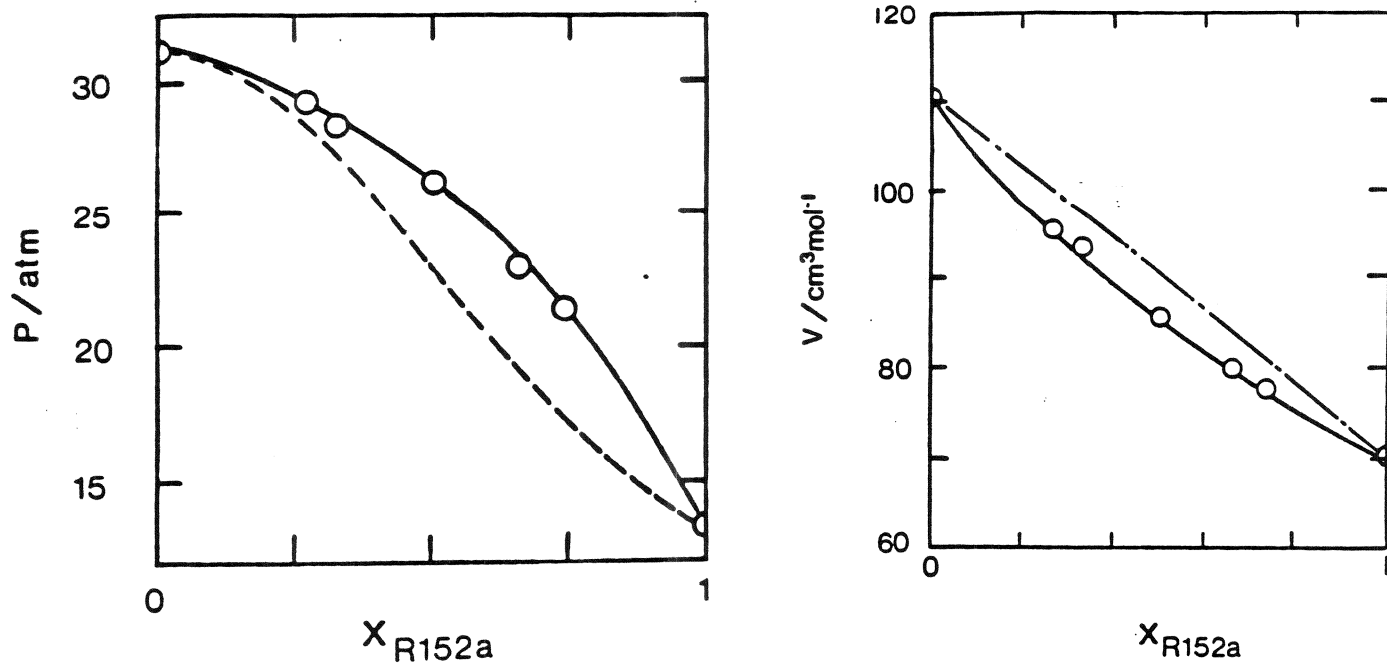


Figure 5. (a) The dew (solid) and bubble (dashed) lines for the mixture R13B1/R152a predicted from the equation of state at a temperature, $T = 55.68\text{ }^{\circ}\text{C}$. The interaction parameter for the mixture was evaluated from data at $15.23\text{ }^{\circ}\text{C}$. (b) The molar volume for the mixture at saturation; the dashed line indicates the linear combination prediction and the solid line the predicted behavior.

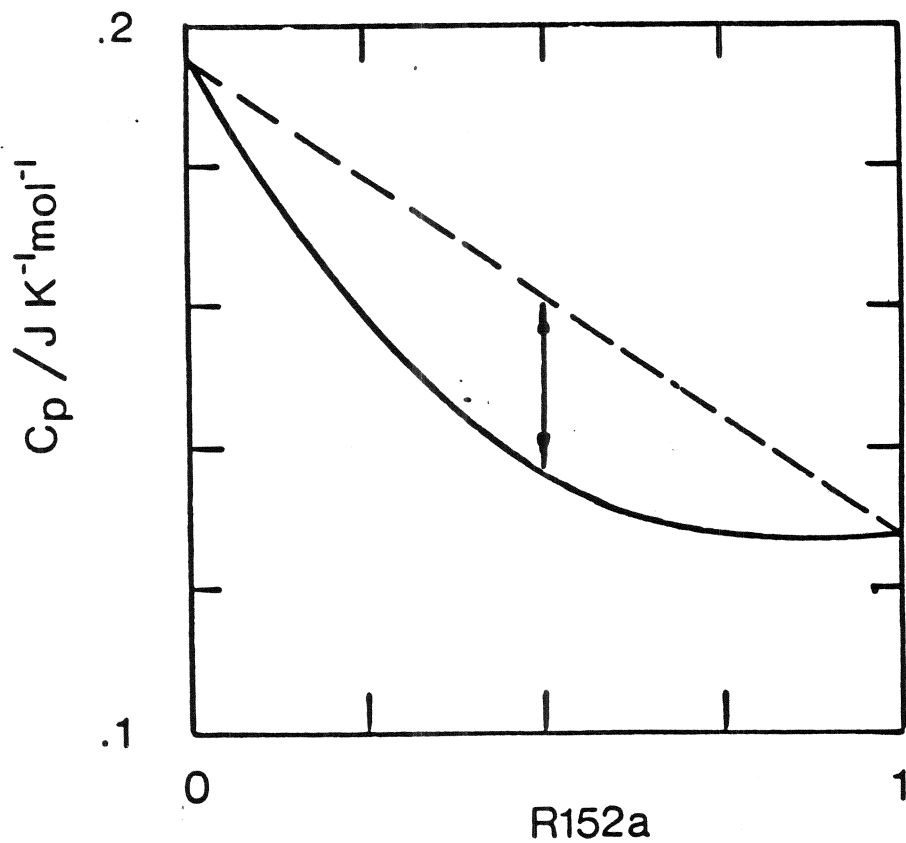


Figure 6. The predicted molar heat capacity at constant pressure for the mixture R13B1/R152a at the saturation pressure of R13B1 and a temperature, $T = 55.68\text{ }^{\circ}\text{C}$.

