

A predictive extended corresponding states model for pure and mixed refrigerants including an equation of state for R134a*†

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We have developed a predictive corresponding states model for the thermophysical properties of pure refrigerants and refrigerant mixtures. The bulk phase properties such as the density, enthalpy and entropy are predicted using the principle of extended corresponding states, incorporating a recent 32-term modified Benedict–Webb–Rubin correlation for the R134a (1,1,1,2-tetrafluoroethane) reference fluid. This theoretically based model uses shape factors to ensure conformality among the various components. A correlation for the shape factors was found by mapping saturation boundaries of the fluids of interest onto the reference fluid and then fitting the results to an empirical correlation. In this work we present the coefficients for density-independent shape-factor correlations for 21 refrigerants, and a set of universal coefficients that can be used with any refrigerant given only the critical parameters and the acentric factor. We show comparisons with experimental density data for each of the 21 refrigerants. We also demonstrate the use of generalized coefficients for shape factors where only the critical parameters and acentric factors are known. In addition, we present comparisons of the volume prediction for two binary refrigerant mixtures and one ternary refrigerant mixture.

(Keywords: refrigerant; R134a; mixture; thermodynamic property; liquid; vapour; change of phase; modelling; calculation)

Modèle thermodynamique prédictif pour les frigorigènes purs et en mélanges, utilisant la méthode des états correspondants et l'équation d'état du R134a

Les auteurs ont mis au point un modèle de prévision des propriétés thermophysiques des frigorigènes purs et en mélanges, par la méthode des états correspondants. On prévoit les propriétés de phase telles que la densité, l'enthalpie et l'entropie en utilisant le principe des états correspondants étendus, qui inclut une corrélation récente, modifiée, de Benedict–Webb–Rubin, à 32 termes pour le R134a (1,1,1,2-tétrafluoroéthane), utilisé comme fluide de référence. Ce modèle théorique utilise des facteurs de forme pour assurer la correspondance entre les divers composants. On a établi une corrélation pour les facteurs de forme en situant les limites de saturation des fluides concernés par rapport au fluide de référence, puis en ajustant les résultats par rapport à une corrélation empirique. Les auteurs présentent les coefficients par corrélation de facteurs de forme indépendants pour la densité, pour 21 frigorigènes, ainsi qu'une série de coefficients universels qui peuvent être utilisés avec n'importe quel frigorigène, en n'utilisant que les paramètres critiques et le facteur acentrique. Sont comparés les résultats avec les valeurs expérimentales pour la densité, pour chacun des 21 frigorigènes. Est décrit également l'utilisation des coefficients généralisés pour les facteurs de forme lorsque seuls les paramètres critiques et le facteur acentrique sont connus. En outre, la prévision du volume est examinée pour deux mélanges binaires et un mélange ternaire de frigorigènes.

(Mots clés: frigorigène; R134a; mélange; propriété thermodynamique; liquide; vapeur; changement de phase; modélisation; calcul)

Many authors have pointed out the need for accurate thermophysical property data and models. Models are especially needed for refrigerant mixtures because of the limited number of experimental studies which have been reported in the literature for these systems. The most accurate approach to modelling properties of single-phase fluid mixtures arises from combining a molecularly

based corresponding states theory with a highly accurate empirical equation of state. This approach eliminates the need for detailed knowledge of the intermolecular potential while retaining the underlying theoretical rigour. In addition, the approach allows for the use of a more complex (and presumably more accurate) mathematical description of the reference fluid *PVT* surface, thereby removing restrictions associated with the inflexible forms of simpler engineering equation of state models.

In this manuscript we discuss the mathematical details, implementation and application of the extended corresponding states model to the equilibrium properties of refrigerants. Transport properties are covered in two

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additional papers^{1,2}. The extended corresponding states theory itself is not new. It was originally proposed by Leland and co-workers^{3,4} in the early 1970s and was used by Rowlinson and co-workers^{5,6} for simple mixtures, by Parrish^{7,8} for liquefied petroleum gas mixtures, and by Mollerup^{9,10} and McCarty¹¹ for cryogenic systems, particularly LNG. More recently, it has been applied to properties of carbon dioxide rich mixtures and air by Ely and co-workers¹²⁻¹⁴. The accuracy of this approach lies in the accuracy of the empirical reference fluid equation of state and in the accuracy of the shape factors which are used in the definition of the equivalent substance state point. In this work we use a recent 32-term Jacobsen-Stewart type modified Benedict-Webb-Rubin (MBWR-32) equation of state for R134a¹⁵ as the reference fluid. Shape factors (discussed below) are found by mapping the saturation boundary of the fluids of interest onto the reference fluid. The results of these mappings were then used to develop a generalized expression for the shape factors of refrigerants relative to the R134a reference. We also present comparisons of the predictions of the model with the PVT surfaces of 21 pure fluid refrigerants. Several mixture volume comparisons are also given.

Model description

Simple corresponding states for pure fluids

The corresponding states principle for simple spherically symmetric pure fluids has been known for many years and is well summarized in several texts^{16,17}. The basic result is that if two pure fluids are conformal (obey the same reduced intermolecular force law), straightforward scaling arguments lead to the conclusion that:

$$a_j^r(\rho_j, T_j) = a_0^r(\rho_0, T_0) \quad (1)$$

In this equation, $a^r = [A(\rho, T) - A^*(\rho, T)]/RT$, where A is the Helmholtz free energy, the asterisk indicates an ideal gas value, ρ is the molar density, T is the absolute temperature, and R is the universal gas constant. The subscript j indicates the fluid of interest and 0 indicates a reference fluid whose thermodynamic properties are known, in principle, with great accuracy. The scaling arguments which lead to Equation (1) provide a relation between the volume and temperature of the fluid j and the corresponding values for the reference fluid, namely $T_0 = T_j/f_j$ and $\rho_0 = \rho_j h_j$. The scale factors f_j and h_j are called the equivalent substance reducing ratios and are related on a microscopic scale to ratios of the intermolecular potential parameters, and on a macroscopic scale, to the critical parameters of the two fluids, namely $f_j = (T_j^c/T_0^c)$ and $h_j = (\rho_0^c/\rho_j^c)$, where the superscript c denotes a critical point value. Other thermodynamic properties of the fluid of interest follow from differentiation of Equation (1). For example, since

$$\begin{aligned} da^r &= d(A^r/RT) \\ &= -\left[\frac{(U-U^*)}{RT^2}\right]dT - \left[\frac{p}{RT} - \frac{1}{V}\right]dV + \sum_{i=1}^n \frac{\hat{\mu}_i - \hat{\mu}_i^*}{RT} dx_i \end{aligned} \quad (2)$$

the residual compressibility factor $z^r = pV/RT - 1$ is

$$z_j^r(\rho_j, T_j) = z_0^r(\rho_j h_j, T_j/f_j) \quad (3)$$

Table 1 Dimensionless residual thermodynamic properties in the extended corresponding states model with density and temperature dependent shape factors

Tableau 1 Propriétés thermodynamiques résiduelles sans dimension dans le modèle par états correspondants étendus avec des facteurs de forme dépendant de la température et de la densité

Property	Relation
Helmholtz free energy	$a_j^r = a_0^r$
Compressibility factor	$z_j^r = z_0^r[1 + H_\rho] + u_0^r F_\rho$
Internal energy	$u_j^r = u_0^r[1 - F_T] - z_0^r H_T$
Entropy	$s_j^r = s_0^r - u_0^r F_T - z_0^r H_T$
Enthalpy	$h_j^r = h_0^r + u_0^r [F_\rho - H_\rho] + z_0^r [H_\rho - H_T]$
Gibbs free energy	$g_j^r = g_0^r + z_0^r H_\rho + u_0^r F_\rho$
Fugacity coefficient	$\ln(f_j/x_0 p) = \ln(f_0/p_0) + z_0^r H_{n_k} + u_0^r F_{n_k}$

The extended corresponding states principle for pure fluids

The formalism discussed above was developed for spherically symmetric molecules whose intermolecular potentials are conformal. This is a limited class of materials that places severe restrictions on the applicability of the model, especially for refrigerants, which are generally non-spherical and polar. In order to overcome this type of problem, Leland and Chappelear³ proposed the use of molecular shape factors. These shape factors are introduced in the equivalent substance reducing ratios for pure fluids and in principle are allowed to be functions of density and temperature. Thus, in effect, we assume that the intermolecular potential parameters are density and temperature dependent, but the potential is itself conformal to the potential of some reference fluid. Mathematically we have $f_j = (T_j^c/T_0^c)\theta(\rho, T)$ and $h_j = (\rho_0^c/\rho_j^c)\phi(\rho, T)$. The parameters θ and ϕ are called shape factors. In the extended corresponding states model, the basic thermodynamic relationship obtained in the simple corresponding states model remains the same:

$$a_j^r(\rho, T_j) = a_0^r(\rho_0, T_0) = a_0^r(\rho_j h_j, T_j/f_j) \quad (4)$$

The thermodynamic relationships between various properties, however, are not those observed in simple corresponding states. Reconsider, for example, the residual compressibility factor, z^r . Allowing for the fact that the shape factors might depend upon density and differentiating Equation (4) with respect to ρ_j we find

$$z_j^r = z_0^r[1 + H_\rho] + u_0^r F_\rho \quad (5)$$

where $u_0^r = (U_0 - U_0^*)/RT_0$, $F_\rho = (\partial f_j/\partial \rho_j)_T (p_j/f_j)$ and $H_\rho = (\partial h_j/\partial \rho_j)_T (p_j/h_j)$. If the shape factors are independent of density then $F_\rho = H_\rho = 0$ and the result from simple corresponding states, $z_j^r = z_0^r$, is retained. Similar relations arise due to the temperature dependence of the shape factors. For example, the dimensionless residual internal energy is given by

$$u_j^r = u_0^r[1 - F_T] - z_0^r H_T \quad (6)$$

where $F_T = (\partial f_j/\partial T_j)_p (T_j/f_j)$ and $H_T = (\partial h_j/\partial T_j)_p (T_j/h_j)$. These results are summarized in Table 1 for other thermodynamic properties of interest.

Extended corresponding states for mixtures

In the case of mixtures, the application of the extended corresponding states model is complicated by the com-

position dependence of the equivalent substance reducing ratios. In our studies we have assumed that this composition dependence is given by the van der Waals one-fluid mixing rules. The van der Waals mixing rules are given by

$$h_x = \sum_{i=1}^n \sum_{j=1}^n x_i x_j h_{ij} \quad (7)$$

and

$$f_x h_x = \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij} h_{ij} \quad (8)$$

The cross terms are obtained from the combining rules:

$$f_{ij} = \sqrt{f_i f_j} (1 - k_{ij}) \quad (9)$$

and

$$h_{ij} = (h_i^{1/3} + h_j^{1/3})^3 (1 - l_{ij})/8 \quad (10)$$

In these equations x_i is the concentration of component i in the mixture, f_x and h_x are the equivalent substance reducing ratios for the mixture and k_{ij} and l_{ij} are the binary interaction parameters that are non-zero when $i \neq j$.

Application of the formulas given in *Table 1* to mixtures requires derivatives of f_x and h_x with respect to temperature, density and composition. An inspection of the mixing rules and the definitions of the equivalent substance reducing ratios shows that the arguments of the shape factors are the effective temperatures and densities of components in the mixture. These, in fact, do not correspond to the temperature and density of the mixture unless the shape factors are identically unity. Thus, in a mixture, the arguments of the shape factors are themselves functions of f_x and h_x . The dependence of these is nominally given by $T_j = T_x f_j / f_x$ and $V_j = V_x h_j / h_x$. Differentiating these relations with respect to T_x we obtain two equations:

$$\begin{aligned} F_x(T_x) &= F_j(T_j)[1 + F_x(T_x) - F_x(T_x)] \\ &\quad + F_j(V_j)[H_j(T_x) - H_x(T_x)] \end{aligned} \quad (11)$$

and

$$\begin{aligned} H_x(T_x) &= H_j(T_j)[1 + F_x(T_x) - F_x(T_x)] \\ &\quad + H_j(V_j)[H_j(T_x) - H_x(T_x)] \end{aligned} \quad (12)$$

where, for example

$$W_\alpha(Y_\beta) = \frac{Y_\beta}{w_\alpha} \frac{\partial w_\alpha}{\partial Y_\beta} \quad \text{and} \quad H_\alpha(T_x) = \frac{T_x}{h_\alpha} \frac{\partial h_\alpha}{\partial T_x} \quad (13)$$

Differentiation of the mixing rules Equations (7) and (8) with respect to temperature, T_x , yields:

$$F_x(T_x) + H_x(T_x) = \frac{1}{f_x h_x} \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij} h_{ij} [F_x(T_x) + \frac{g_i}{g_{ij}} H_x(T_x)] \quad (14)$$

and

$$H_x(T_x) = \frac{1}{h_x} \sum_{i=1}^n \sum_{j=1}^n x_i x_j h_{ij} \frac{g_i}{g_{ij}} H_x(T_x) \quad (15)$$

where $g_i = h_i^{1/3}$ and $g_{ij} = (g_i + g_j)/2$.

Simultaneous solution of Equations (11) and (12) for $F_x(T_x)$ and $H_x(T_x)$ and substitution into Equations (14) and (15) and subsequent solution for $F_x(T_x)$ and $H_x(T_x)$ yields $F_x(T_x) = 1 - S_7/R$ and $H_x(T_x) = S_6/R$. Similar procedures yield for the volume derivatives $F_x(V_x) = (S_2 + S_4 - S_7)/R$ and $H_x(V_x) = (S_6 + S_1 - S_3 + R)/R$; for the composition derivatives $F_x(n_k) = [S_5^{(k)} S_7 - S_8^{(k)} (S_2 + S_4)]/R$ and $H_x(n_k) = [S_8^{(k)} (S_1 + S_3) - S_5^{(k)} S_6]/R$ where $R = (S_1 + S_3)S_7 - (S_2 + S_4)S_6$. The definitions of the sums S_m which appear in these results are given below:

$$S_1 = \frac{1}{f_x h_x} \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij} h_{ij} [1 - H_i(V_i)] D_i \quad (16)$$

$$S_2 = \frac{1}{f_x h_x} \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij} h_{ij} F_i(V_i) D_i \quad (17)$$

$$S_3 = \frac{1}{f_x h_x} \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij} h_{ij} \frac{g_i}{g_{ij}} H_i(T_i) D_i \quad (18)$$

$$S_4 = \frac{1}{f_x h_x} \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij} h_{ij} \frac{g_i}{g_{ij}} [1 - F_i(T_i)] D_i \quad (19)$$

$$S_5^{(k)} = \frac{2x_k}{f_x h_x} \sum_{i=1}^n x_i f_{ik} h_{ik} \quad (20)$$

$$S_6 = \frac{1}{h_x} \sum_{i=1}^n \sum_{j=1}^n x_i x_j h_{ij} \frac{g_i}{g_{ij}} H_i(T_i) D_i \quad (21)$$

$$S_7 = \frac{1}{h_x} \sum_{i=1}^n \sum_{j=1}^n x_i x_j h_{ij} \frac{g_i}{g_{ij}} [1 - F_i(T_i)] D_i \quad (22)$$

$$S_8^{(k)} = \frac{2x_k}{h_x} \sum_{i=1}^n x_i h_{ik} \quad (23)$$

where

$$D_i = [(1 - H_i(V_i)) (1 - F_i(T_i)) - F_i(V_i) H_i(T_i)]^{-1} \quad (24)$$

Results

The reference fluid

The reference fluid used in this work is R134a. The form of equation of state used to represent the reference fluid is the Jacobsen-Stewart¹⁸ modified 32-term BWR equation (MBWR-32). This equation has been used extensively to represent the properties of hydrocarbons and common inorganics. Its functional form is a polynomial in density and temperature and is given by

$$p = \sum_{n=1}^9 a_n(T) \rho^n + e^{-(\rho/\rho_0)^2} \sum_{n=10}^{15} a_n(T) \rho^{2n-17} \quad (25)$$

The temperature dependence of the $a_n(T)$ is summarized in *Table 2*.

MBWR-32 equation of state coefficients for R134a were first given by McLinden *et al.*¹⁹ Recently, due to the

Table 2 Temperature dependence of the MBWR-32 coefficients
Tableau 2 Effet de la température sur les coefficients MBWR32

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

Table 3 Reference fluid equation of state coefficients (p , bar; ρ mol 1^{-1} ; T , K)
Tableau 3 Coefficients de l'équation d'état du fluide de référence

b_1	$+9.652\ 093\ 62 \times 10^{-2}$	b_{17}	$-7.330\ 501\ 88 \times 10^{-3}$
b_2	$-4.018\ 247\ 699$	b_{18}	$+3.806\ 559\ 64$
b_3	$+3.952\ 395\ 33 \times 10^1$	b_{19}	$-1.058\ 320\ 88 \times 10^{-1}$
b_4	$+1.345\ 328\ 69 \times 10^3$	b_{20}	$-6.792\ 430\ 84 \times 10^5$
b_5	$-1.394\ 397\ 41 \times 10^6$	b_{21}	$-1.269\ 983\ 79 \times 10^8$
b_6	$-3.092\ 813\ 55 \times 10^{-3}$	b_{22}	$-4.262\ 344\ 32 \times 10^4$
b_7	$+2.923\ 814\ 12$	b_{23}	$+1.019\ 733\ 38 \times 10^9$
b_8	$-1.651\ 466\ 14 \times 10^3$	b_{24}	$-1.866\ 995\ 27 \times 10^2$
b_9	$+1.507\ 060\ 03 \times 10^6$	b_{25}	$-9.334\ 263\ 23 \times 10^4$
b_{10}	$+5.349\ 739\ 48 \times 10^{-5}$	b_{26}	$-5.717\ 352\ 09$
b_{11}	$+5.439\ 333\ 18 \times 10^{-1}$	b_{27}	$-1.767\ 627\ 39 \times 10^5$
b_{12}	$-2.113\ 260\ 50 \times 10^2$	b_{28}	$-3.972\ 827\ 52 \times 10^{-2}$
b_{13}	$-2.681\ 912\ 04 \times 10^{-2}$	b_{29}	$+1.430\ 168\ 45 \times 10^1$
b_{14}	$-5.410\ 671\ 26 \times 10^{-1}$	b_{30}	$+8.030\ 852\ 94 \times 10^{-5}$
b_{15}	$-8.517\ 317\ 79 \times 10^2$	b_{31}	$-1.719\ 590\ 74 \times 10^{-1}$
b_{16}	$+2.051\ 882\ 54 \times 10^{-1}$	b_{32}	$+2.262\ 383\ 86$
R	$0.831\ 447\ 10 \times 10^{-1}$	ω	$0.326\ 680\ 00$

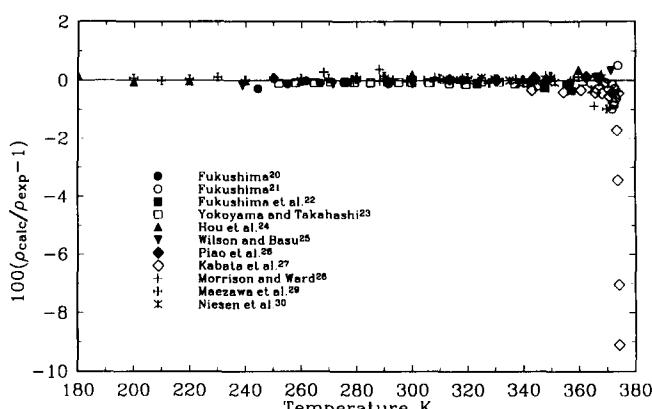


Figure 1 Comparison of experimental results with saturated liquid density calculated with MBWR-32 equation of state for R134a
Figure 1 Comparaison des données expérimentales avec la densité de liquide saturé calculée avec l'équation d'état MBWR-32 pour le R134a

availability of new data, the R134a surface has been refitted¹⁵. The coefficients are given in *Table 3*. Also given in *Table 3* are the gas constant, R , and the value of the Pitzer acentric factor, ω . In addition, we used¹⁵: $T_c = 374.179$ K (IPTS 90), $P_c = 4.056$ MPa and $\rho_c = 5.0308$ mol/l. *Figures 1* and *2* show the percentage deviation in density calculation against the temperature for the saturated liquid and the saturated vapour, respectively. *Figure 3* compares the calculated and experimental vapour pressures. The equation of state is valid

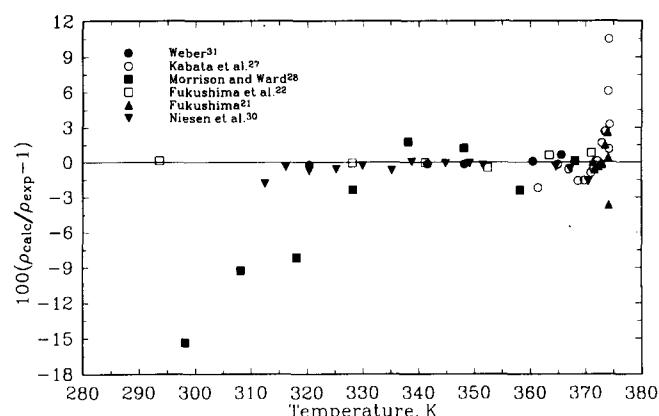


Figure 2 Comparison of experimental results with saturated vapour density calculated with MBWR-32 equation of state for R134a
Figure 2 Comparaison des données expérimentales avec la densité de vapeur saturée calculée avec l'équation d'état MBWR-32 pour le R134a

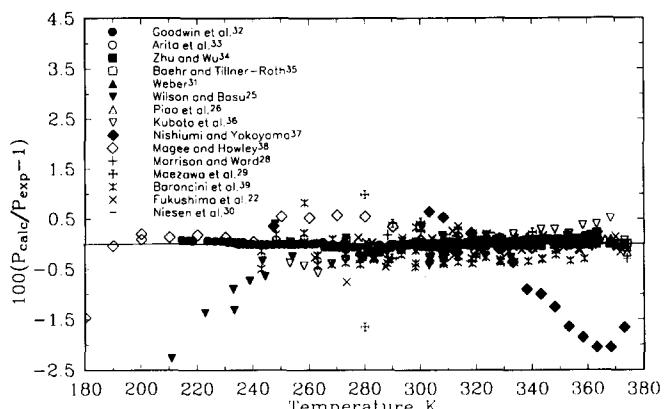


Figure 3 Comparison of experimental results with vapour pressures calculated with MBWR-32 equation of state for R134a
Figure 3 Comparaison des données expérimentales avec les pressions de vapeur calculées avec l'équation d'état MBWR-32 pour le R134a

for both liquid and vapour phases at pressures up to 70 MPa, and for temperatures from the triple point, 169.854 K (IPTS 90)⁴⁰, to 450 K. The equation of state typically reproduces the pressure within 0.4% and density within 0.2%. Exceptions are large density deviations in the near critical region, and large pressure errors in the low-temperature compressed liquid region close to the saturation boundary. Comparisons of experimental and calculated densities for selected data sets as a function of temperature and density are shown in *Figures 4* and *5*. *Figure 6* shows a comparison of experimental and calculated heat capacity at constant volume as a function of temperature for the liquid data set of Magee⁴⁰; the calculated values of C_v are within 1.5%. *Figure 7* compares experimental and calculated heat capacity at constant pressure. The results for C_p are within 2.0%. Ideal gas heat capacities were computed using a correlation in Ref. 19. *Figure 8* compares the experimental and calculated second virial coefficients, which are predicted to within about 2%. *Figure 9* shows a comparison of experimental and calculated sound speed w , as a function of temperature. The three data sets shown are in the liquid region, and the correlation predicts sound speed in this region to within 3%.

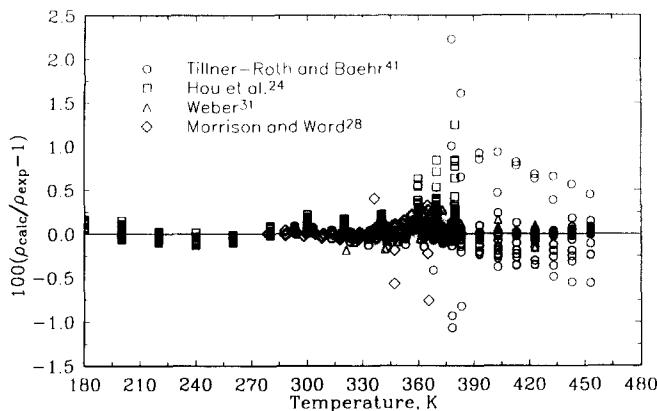


Figure 4 Comparison of experimental and calculated density for R134a as a function of temperature for selected PVT data sets
Figure 4 Comparaison des données expérimentales avec la densité du R134a, calculée en fonction de la température pour plusieurs valeurs PVT

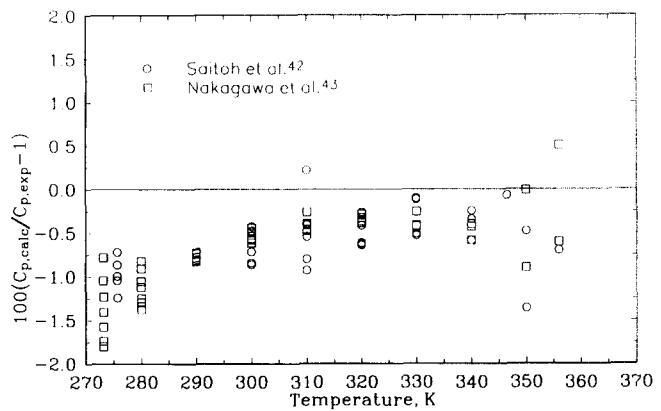


Figure 7 Comparison of experimental and calculated C_p for R134a
Figure 7 Comparaison des données expérimentales avec la valeur calculée de la chaleur massique du R134a à pression constante

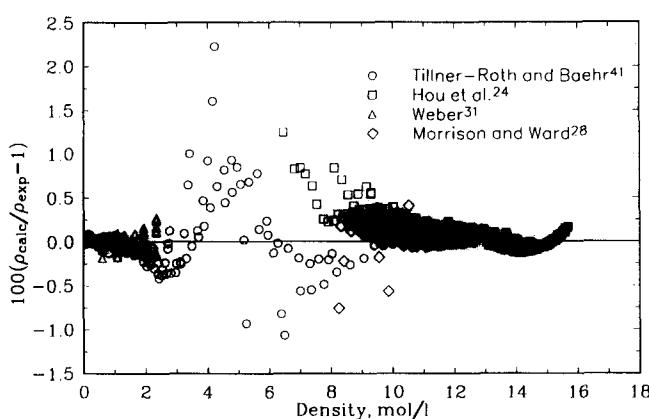


Figure 5 Comparison of experimental and calculated density for R134a as a function of density for selected PVT data sets
Figure 5 Comparaison des données expérimentales avec le densité du R134a, calculée en fonction de la température pour plusieurs valeurs PVT

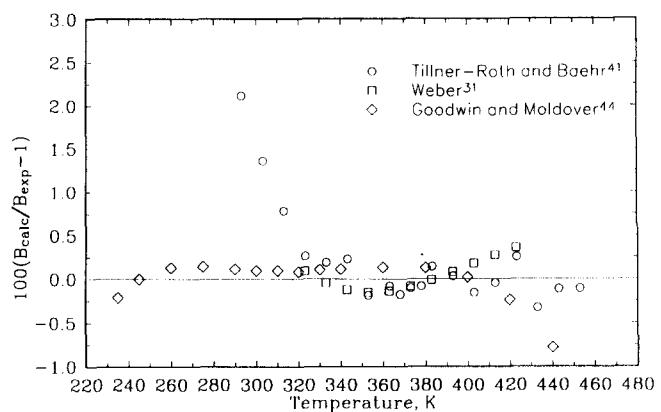


Figure 8 Comparison of experimental and calculated second virial coefficients for R134a
Figure 8 Comparaison des données expérimentales avec les coefficients viriels secondaires pour le R134a

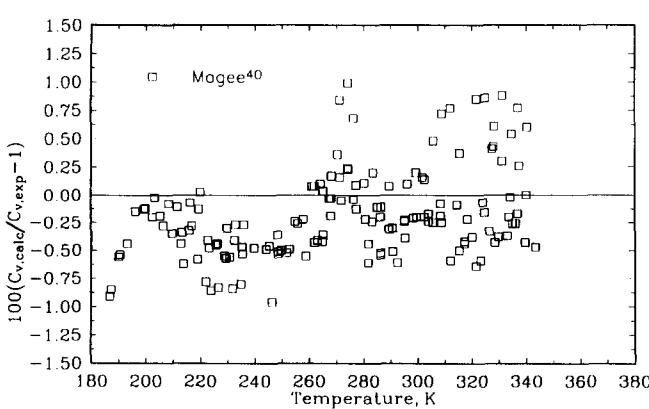


Figure 6 Comparison of experimental and calculated C_v for R134a
Figure 6 Comparaison des données expérimentales avec la valeur calculée de la chaleur massique du R134a à volume constant

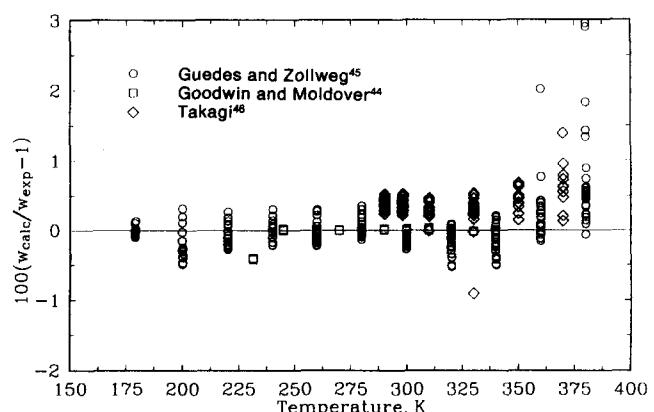


Figure 9 Comparison of experimental and calculated sound speed for R134a
Figure 9 Comparaison des données expérimentales avec les valeurs calculées de la vitesse du son du R134a

Table 4 Summary of references used in vapour pressure and saturated liquid density fits
Tableau 4 Condensé des références utilisées pour corréliser la pression de vapeur et la densité du liquide saturé

Fluid	Vapour pressure references	Saturated liquid density references
R11	Osborne <i>et al.</i> ⁴⁸ , Benning and McHarness ⁴⁹ , Jaeger ⁵⁰ , Kletskii ⁵¹ , Fernandez-Fassnacht and del Rio ⁵²	Benning and McHarness ⁵³ , Kremenevskaya and Rivkin ⁵⁴ , Altunin <i>et al.</i> ⁵⁵ , Chavez <i>et al.</i> ⁵⁶
R12	Fernandez-Fassnacht and del Rio ⁵⁷ , Jaeger ⁵⁰ , Kumagai and Iwasaki ⁵⁸ , Takaishi <i>et al.</i> ⁵⁹ , McHarness <i>et al.</i> ⁶⁰ , Kells <i>et al.</i> ⁶¹ , Michels <i>et al.</i> ⁶² , Watanabe <i>et al.</i> ⁶³	Bichowsky and Gilkey ⁶⁴ , Jaeger ⁵⁰ , Kumagai and Iwasaki ⁵⁸ , Takaishi <i>et al.</i> ⁵⁹ , McHarness <i>et al.</i> ⁶⁰
R13	Fernandez-Fassnacht and del Rio ⁵⁷ , Jaeger ⁵⁰ , Albright and Martin ⁶⁵ , Oguchi <i>et al.</i> ⁶⁶ , Thornton <i>et al.</i> ⁶⁷	Albright and Martin ⁶⁸ , Shavandrin and Li ⁶⁸ , Oguchi <i>et al.</i> ⁶⁶
R13b1	Jaeger ⁵⁰ , Perelshtein and Aleshin ⁶⁹	Jaeger ⁵⁰ , Higashi <i>et al.</i> ⁷⁰
R14	Simon <i>et al.</i> ⁷¹ , Smith and Pace ⁷² , Menzel and Mohry ⁷³ , Enokido <i>et al.</i> ⁷⁴	Shinsaka <i>et al.</i> ⁷⁵ , Knobler and Pings ⁷⁶ , Terry <i>et al.</i> ⁷⁷ , Tremaine and Robinson ⁷⁸
R22	Niesen <i>et al.</i> ³⁰ , Kletskii ⁷⁹ , Zander ⁸⁰ , Kohlen <i>et al.</i> ⁸¹ , Jaeger ⁵⁰ , Benning and McHarness ⁴⁹ , Kumagai and Iwasaki ⁵⁸ , Takaishi <i>et al.</i> ⁵⁹ , Lagutina ⁸² , Oguchi <i>et al.</i> ⁸³	Niesen <i>et al.</i> ³⁰ , Zander ⁸⁰ , Okada <i>et al.</i> ⁸⁴ , Kohlen <i>et al.</i> ⁸¹ , Higashi <i>et al.</i> ⁸⁵ , Kumagai and Iwasaki ⁵⁸ , Takaishi <i>et al.</i> ⁵⁹ , Oguchi <i>et al.</i> ⁸³ , Benning and McHarness ⁵³
R23	Wagner ⁸⁶ , Hou and Martin ⁸⁷ , Hori <i>et al.</i> ⁸⁸ , Popowicz <i>et al.</i> ⁸⁹ , Valentine <i>et al.</i> ⁹⁰	Döring and Loeffler ⁹¹ , Hou and Martin ⁸⁷ , Shinsaka <i>et al.</i> ⁷⁵ , Shavandrin <i>et al.</i> ⁹²
R32	Malbrunot <i>et al.</i> ⁹³ , Weber and Goodwin ⁹⁴ , Niesen <i>et al.</i> ⁹⁵ , Kanungo <i>et al.</i> ⁹⁶	Malbrunot <i>et al.</i> ⁹³ , Kanungo <i>et al.</i> ⁹⁶ , Shinsaka <i>et al.</i> ⁷⁵ , Niesen <i>et al.</i> ⁹⁵
R113	Mastroianni <i>et al.</i> ⁹⁷ , Benning and McHarness ⁴⁹ , Hiraoka and Hildebrand ⁹⁸ , Hovorka and Geiger ⁹⁹ , Riedel ¹⁰⁰	Mastroianni <i>et al.</i> ⁹⁷ , Hovorka and Geiger ⁹⁹ , Benning and McHarness ⁵³
R114	Thornton <i>et al.</i> ⁶⁷ , Wilson and Hules ¹⁰¹ , Martin ¹⁰² , Hasegawa <i>et al.</i> ¹⁰³	Wilson and Hules ¹⁰¹ , Martin ¹⁰² , Higashi <i>et al.</i> ¹⁰⁴
R115	Mears <i>et al.</i> ¹⁰⁵ , Aston <i>et al.</i> ¹⁰⁶	Mears <i>et al.</i> ¹⁰⁵
R123	Weber ¹⁰⁷ , Kubota <i>et al.</i> ¹⁰⁸ , Yamashita <i>et al.</i> ¹⁰⁸ , Maezawa <i>et al.</i> ²⁹ , Oguchi <i>et al.</i> ¹⁰⁹ , Weber ¹¹⁶ , Piao <i>et al.</i> ¹¹⁰	Schmidt ¹¹¹ , Morrison and Ward ²⁸ , Weber and Levelt Sengers ¹¹² , Oguchi and Takaishi ¹¹³ , Tanikawa <i>et al.</i> ¹¹⁴ , Maezawa <i>et al.</i> ²⁹ , Richard and Orfeo ¹¹⁵ , Fukushima <i>et al.</i> ²²
R124	Kubota <i>et al.</i> ¹¹⁶ , Shankland <i>et al.</i> ¹¹⁷ , Niesen <i>et al.</i> ³⁰	Kubota <i>et al.</i> ¹¹⁶ , Shankland <i>et al.</i> ¹¹⁷ , Niesen <i>et al.</i> ³⁰
R125	Shankland <i>et al.</i> ¹¹⁸ , Wilson <i>et al.</i> ¹¹⁹	Shankland <i>et al.</i> ¹¹⁸ , Defibaugh and Morrison ¹²⁰
R134	Ward and Morrison ¹²¹ , Maezawa <i>et al.</i> ¹²²	Ward and Morrison ¹²¹ , Maezawa <i>et al.</i> ¹²²
R141b	Weber ¹²³ , Morrison ¹²⁴ , Weber ¹²⁵ , Defibaugh <i>et al.</i> ¹²⁶ , Maezawa <i>et al.</i> ¹²²	Morrison ¹²⁴ , Richard and Orfeo ¹²⁷ , Defibaugh <i>et al.</i> ¹²⁶ , Maezawa <i>et al.</i> ¹²²
R142b	Maezawa <i>et al.</i> ¹²⁸ , Mears <i>et al.</i> ¹²⁹ , Cherneeva ¹³⁰ , Riedel ¹³¹	Maezawa <i>et al.</i> ¹²⁸ , Mears <i>et al.</i> ¹²⁹ , Cherneeva ¹³⁰ , Valtz <i>et al.</i> ¹³² , Riedel ¹³¹
R143a	Russell <i>et al.</i> ¹³³ , Mears <i>et al.</i> ¹²⁹	Russell <i>et al.</i> ¹³³ , Mears <i>et al.</i> ¹²⁹ , Yokoyama and Takahashi ²³
R152a	Higashi <i>et al.</i> ¹³⁴ , Mears <i>et al.</i> ¹²⁹ , Yada <i>et al.</i> ¹³⁵ , Iso and Uematsu ¹³⁶ , Zhao <i>et al.</i> ¹³⁹ , Blancke and Weiß ¹⁴⁰ , Baehr and Tillner-Roth ³⁵ , Geller <i>et al.</i> ¹⁴¹	Sato <i>et al.</i> ¹³⁷ , Higashi <i>et al.</i> ¹³⁴ , Masui <i>et al.</i> ¹³⁸ , Mears <i>et al.</i> ¹²⁹ , Iso and Uematsu ¹³⁶ , Blanke and Weiß ¹⁴⁰
R218	Brown ¹⁴²	Brown ¹⁴²
RC270	Lin <i>et al.</i> ¹⁴³ , Ruehrwein and Powell ¹⁴⁴ , Lin <i>et al.</i> ¹⁴⁵ , Booth and Morris ¹⁴⁶ , Haselden and Snowden ¹⁴⁷	Lin <i>et al.</i> ¹⁴³ , Lin <i>et al.</i> ¹⁴⁵

The deviations are greatest as the critical region is approached.

Shape factor correlations

Application of the extended corresponding states model in a predictive mode requires a knowledge of a component's shape factors given a relatively small amount of information: for example, the critical point parameters and perhaps the acentric factor. To develop such a correlation, we would ideally use high-accuracy equations of state and broadly based experimental data for homologous series in conjunction with the results given in *Table 1* to calculate 'exact' shape factors. These could then be correlated in terms of appropriately reduced variables. Unfortunately, the 'super' equations of state which are necessary to perform this mapping are not yet readily available for refrigerants, especially the HFCs.

Currently, most of the data which are available for refrigerants are for the saturation boundary – the vapour pressures and saturated liquid densities. According to the results given in *Table 1*, these properties are related to the reference fluid properties through the equations

$$p_j^s(T) = p_0^s(T/f_j)f_j/h_j \quad (26)$$

and

$$\rho_j^s(T) = \rho_0^s(T/f_j)h_j \quad (27)$$

where the superscript s denotes evaluation along the saturation boundary. Simultaneous solution of these two equations provides the equivalent substance reducing ratios along the saturation boundary. Since the saturation boundary only depends upon temperature, all of the density derivatives given in *Table 1* are identically zero.

Solution of Equations (26) and (27) requires that experimental saturation data for the fluids of interest be fitted to predetermined functional forms. The vapour pressures were fitted to the Frost–Kalkwarf–Thodos⁴⁷ equation:

$$\ln(P) = \alpha_1 - \alpha_2/T + \alpha_3 \ln(T) + \alpha_4 P/T^2 \quad (28)$$

which was chosen because it has the ability to simultaneously fit both high- and low-temperature data. The liquid densities were fitted to a function proposed by Ely *et al.*¹²:

$$\frac{\rho^s}{\rho^e} - 1 = \frac{k_1 \tau^\beta + k_2 \tau^2 + k_3 \tau^3}{1 + k_4 \tau^{1-\beta}} \quad (29)$$

where $T_r = T/T_c$ and $\tau = 1 - T_r$. The experimental data used to fit the vapour pressure and saturated liquid densities are summarized in *Table 4*. The data points

Table 5 Coefficients for shape factor correlations

Tableau 5 Coefficients pour les corrélations de facteurs de forme

Fluid	α_1	α_2	β_1	β_2
R115	0.160 57	-0.512 83	-0.939 68	0.382 60
R142b	0.599 96 $\times 10^{-1}$	-0.648 52	-0.432 34	0.215 89
R141b	0.158 45	-0.536 89	-0.103 35 $\times 10^1$	0.234 58
R114	0.109 04	-0.630 03	-0.786 79	0.451 37
R23	-0.401 79 $\times 10^{-1}$	-0.732 73	0.277 21	0.736 06 $\times 10^{-1}$
R113	0.889 41 $\times 10^{-1}$	-0.628 28	-0.718 51	0.408 16
R22	0.602 50 $\times 10^{-1}$	-0.672 42	-0.527 04	0.768 56 $\times 10^{-1}$
R11	0.850 40 $\times 10^{-1}$	-0.540 13	-0.301 81	0.202 91
R12	0.684 87 $\times 10^{-1}$	-0.604 24	-0.317 91	0.212 30
R13	0.877 65 $\times 10^{-1}$	-0.518 95	-0.278 86	0.192 27
R13b1	0.474 64 $\times 10^{-1}$	-0.689 68	-0.284 77	0.429 61
R14	0.107 22	-0.552 28	-0.540 55	0.288 14
R152a	-0.823 96 $\times 10^{-1}$	-0.683 04	0.737 78	-0.268 55
R123	0.128 55	-0.582 64	-0.748 18	0.458 55
R124	0.165 93	-0.545 57	-0.959 09	0.732 63
R134	0.158 35	-0.529 73	-0.625 16	0.858 32
R143a	-0.228 07 $\times 10^{-1}$	-0.647 46	0.365 63	-0.260 04 $\times 10^{-1}$
R125	0.277 72	-0.495 66	-0.131 12 $\times 10^1$	0.181 91 $\times 10^1$
R218	0.648 45 $\times 10^1$	-0.394 48	-0.442 79 $\times 10^2$	0.362 67 $\times 10^2$
R32	-0.236 43	-0.825 60	0.146 68 $\times 10^1$	-0.805 00
RC270	0.364 05 $\times 10^{-1}$	-0.692 58	-0.209 74	0.137 69

Table 6 Constants used in shape factor correlations

Tableau 6 Constantes utilisées dans les corrélations des facteurs de forme

Fluid	ω	T_c (K)	P_c (MPa)	V_c (l mol $^{-1}$)
R115	0.252 26	0.353 09 $\times 10^3$	0.315 50 $\times 10^1$	0.251 70
R142b	0.237 33	0.410 30 $\times 10^3$	0.412 00 $\times 10^1$	0.226 40
R141b	0.218 24	0.481 50 $\times 10^3$	0.454 00 $\times 10^1$	0.251 99
R114	0.256 84	0.418 85 $\times 10^3$	0.326 27 $\times 10^1$	0.293 00
R23	0.264 70	0.299 20 $\times 10^3$	0.484 33 $\times 10^1$	0.133 00
R113	0.254 68	0.487 25 $\times 10^3$	0.341 47 $\times 10^1$	0.325 00
R22	0.230 33	0.369 20 $\times 10^3$	0.509 16 $\times 10^1$	0.165 00
R11	0.180 80	0.471 20 $\times 10^3$	0.434 18 $\times 10^1$	0.248 00
R12	0.175 37	0.385 00 $\times 10^3$	0.408 34 $\times 10^1$	0.217 00
R13	0.162 55	0.302 00 $\times 10^3$	0.379 97 $\times 10^1$	0.180 00
R13b1	0.166 53	0.340 20 $\times 10^3$	0.397 19 $\times 10^1$	0.200 00
R14	0.176 07	0.227 60 $\times 10^3$	0.373 42 $\times 10^1$	0.140 00
R152a	0.269 49	0.386 70 $\times 10^3$	0.449 20 $\times 10^1$	0.181 00
R123	0.282 33	0.456 94 $\times 10^3$	0.367 40 $\times 10^1$	0.278 00
R124	0.286 09	0.395 65 $\times 10^3$	0.364 00 $\times 10^1$	0.243 70
R134	0.285 74	0.392 10 $\times 10^3$	0.456 20 $\times 10^1$	0.189 29
R143a	0.255 40	0.346 30 $\times 10^3$	0.376 00 $\times 10^1$	0.194 00
R125	0.303 44	0.339 40 $\times 10^3$	0.363 10 $\times 10^1$	0.210 01
R218	0.325 00	0.345 10 $\times 10^3$	0.268 00 $\times 10^1$	0.299 80
R32	0.276 27	0.351 60 $\times 10^3$	0.683 00 $\times 10^1$	0.120 80
RC270	0.130 29	0.398 30 $\times 10^3$	0.557 95 $\times 10^1$	0.163 00

were not all given equal weights. The shape factors determined by mapping the saturation boundaries were used to develop generalized correlations which only require a knowledge of the Pitzer acentric factor ω ($\omega \equiv -1.0 - \log_{10}(P_{\text{sat}}/P_c)_{T_r=0.7}$) and critical point constants. The functional forms of these correlations are

$$\theta_i = 1 + (\omega_i - \omega_0)(\alpha_1 + \alpha_2 \ln T_r) \quad (30)$$

and

$$\phi_i = \frac{Z_i^c}{Z_i} [1 + (\omega_i - \omega_0)(\beta_1 + \beta_2 \ln T_r)] \quad (31)$$

These functional forms were chosen so that the correlated shape factors would extrapolate smoothly into the one-phase region. The coefficients (α_1 , α_2 , β_1 , β_2) and

constants (ω , T_c , P_c , V_c) for each of the fluids are given in Tables 5 and 6.

It is useful to have a universal set of coefficients for the shape factor correlations that could be used for a refrigerant that does not appear in Tables 5 and 6. All that would be required are the critical parameters and the acentric factor. Data from the following 10 fluids were used to develop generalized coefficients for a correlation for the shape factors of refrigerants with R134a as a reference fluid: {R11, R12, R13, R22, R113, R114, R123, R125, R142b}. First the correlations used for saturated liquid density and vapour pressures were used along with Equations (26) and (27) to generate the θ shape factor for the 10 fluids listed. These values of the shape factor as a function of temperature were then fitted to the form of Equation (30) over a reduced temperature range 0.35–0.95, and the following coefficients were found:

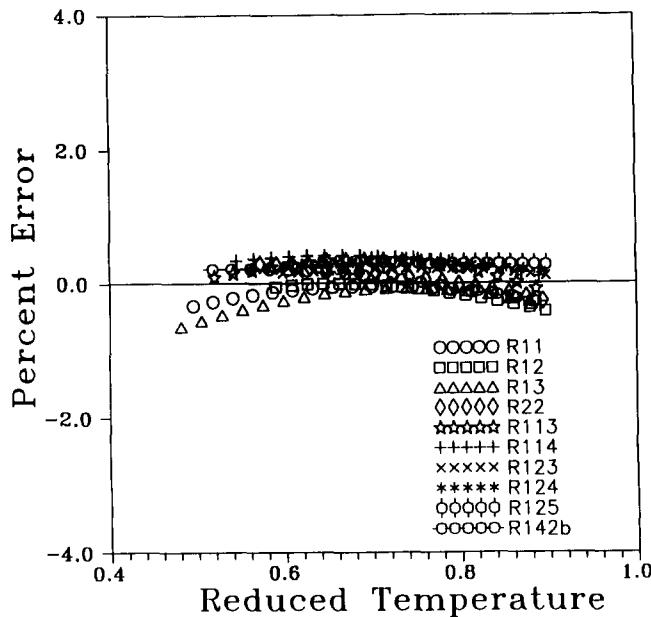


Figure 10 Comparison of universal and fitted θ shape factors for 10 refrigerants

Figure 10 Comparaison des facteurs de forme θ universels et corrélés, pour 10 frigorifères

$$\alpha_1 = 0.086\,853\,583\,565 \quad \alpha_2 = -0.559\,450\,946\,28 \quad (32)$$

Figure 10 illustrates the deviations of the θ shape factor determined with the generalized coefficients, Equations (30)–(33), and those found by mapping the saturation boundary for each individual fluid, Equation (26) and (27), for 10 different refrigerants. The results are quite satisfactory, with average absolute deviations generally within 1% for θ .

To obtain generalized coefficients for the ϕ shape factor, the coefficients found for the generalized θ , Equations (30) and (32), were used along with the vapour pressure, saturated liquid density correlations, and Equations (26) and (27) to generate the ϕ shape factors as a function of temperature. This use of correlated (rather than calculated) θ shape factors provides optimal values for use in the generalization. The results of the ϕ fit were:

$$\beta_1 = 0.057\,382\,113\,745 \quad \beta_2 = 0.201\,640\,939\,38 \quad (33)$$

The fits in this case were from a reduced temperature of 0.35–0.85. The ϕ shape factor sometimes showed a hook at the higher reduced temperatures, perhaps due to uncertainty in the critical parameters, and it was felt best to fit only to a reduced temperature of 0.85 to avoid the ‘hook’. Figure 11 shows the deviations of the ϕ shape factor determined with the generalized coefficients, Equations (31) and (33), and the optimal correlated ϕ described above, for 10 different refrigerants. The results for the ϕ shape factors, although not as good as the results for θ , are satisfactory, with average absolute deviations generally within 2%. The ϕ shape factor is very sensitive to the values of the critical point parameters. In particular, the systematic offsets for some of the fluids can be directly attributed to the critical compressibility factor ratio which appears in Equation (31). Errors of a few cubic decimetres per mol in the critical volume can cause this ratio to change substantially.

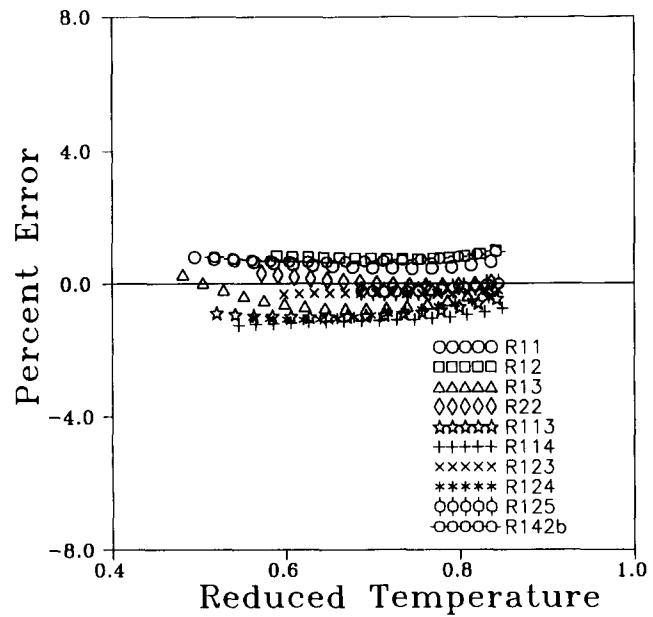


Figure 11 Comparison of universal and fitted ϕ shape factors for 10 refrigerants

Figure 11 Comparaison des facteurs de forme θ universels et corrélés, pour 10 frigorifères

Pure fluid PVT results

Comparisons with experimental density data were made with the model predictions using the shape factor correlations of Tables 5 and 6. The results of these comparisons for 21 fluids are given in Table 7. We use the definitions:

$$Aad = \sum_{i=1}^n \frac{\text{Abs}[100(\rho^{\text{calc}} - \rho^{\text{exp}})/\rho^{\text{exp}}]}{n} \quad (34)$$

$$\text{Bias} = \sum_{i=1}^n \frac{100(\rho^{\text{calc}} - \rho^{\text{exp}})/\rho^{\text{exp}}}{n} \quad (35)$$

$$\text{RMS} = \left[\sum_{i=1}^n \frac{[100(\rho^{\text{calc}} - \rho^{\text{exp}})/\rho^{\text{exp}}]^2}{n} - \text{bias}^2 \right]^{1/2} \quad (36)$$

In general, the data cover both the saturated and compressed liquid as well as dense gas regions, although for some fluids very few data points are available. In addition, data near critical in the region $0.97 < T/T_c < 1.03$ have been excluded. Density predictions near critical can have very large deviations. With the exception of R218, all of the fluids have an average absolute deviation of less than 3% for the entire range of conditions excluding critical. For several fluids such as R32, R218, R143a and R152a the large root mean square (RMS) error shows that there is a lot of scatter in the data themselves.

Figures 12 and 13 show the nature of the density deviations as a function of temperature and pressure for R22. The data in this case are from 10 different sources covering the compressed liquid and dense gas regions. The density predictions shown here for R22 are good, with average absolute density deviations of 0.59% (excluding the near-critical region). The large deviations as the critical region is approached are indicated. When the near critical points are included, the average absolute devi-

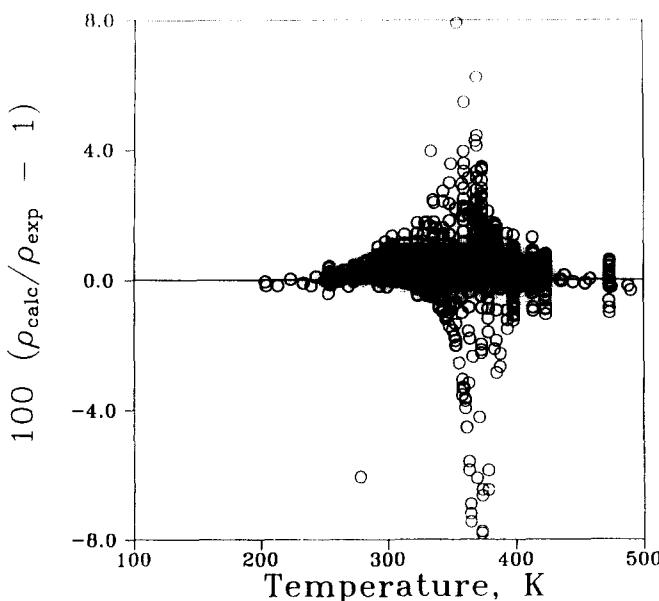


Figure 12 Comparison of experimental and calculated density for R22 as a function of temperature

Figure 12 Comparaison des valeurs expérimentales et de la densité du R22 calculée en fonction de la température

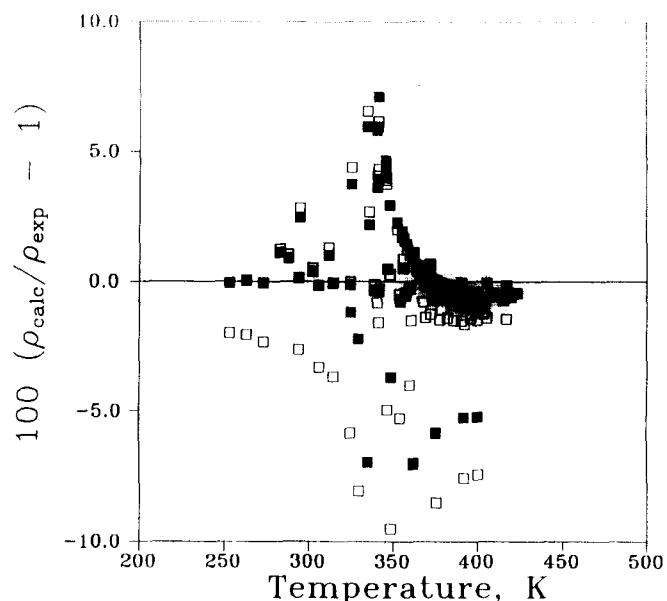


Figure 14 Comparison of experimental and calculated density for R13b1 as a function of temperature. Filled squares calculated using optimal shape factor coefficients for R13b1, open squares calculated using universal shape factor coefficients

Figure 14 Comparaison des valeurs expérimentales et de la densité du R13b1 calculée en fonction de la température. Les carrés noirs représentent les valeurs calculées avec des coefficients de facteur de forme optimaux pour le R13b1, et les carrés blancs représentent des coefficients de facteur de forme universels

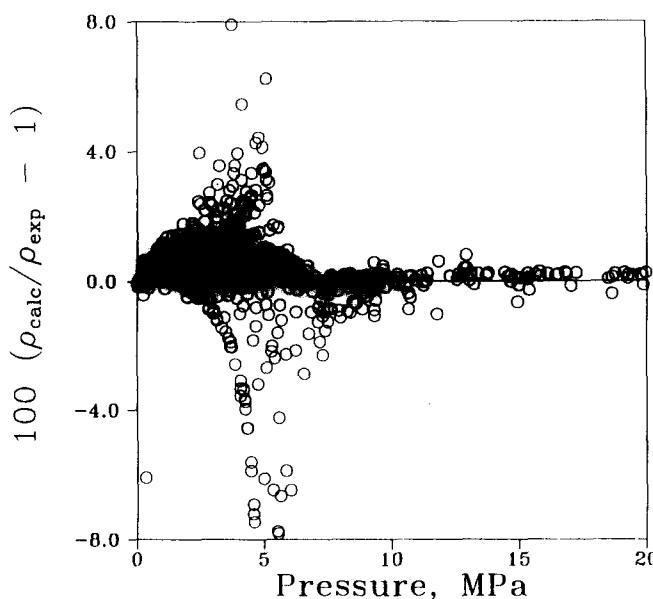


Figure 13 Comparison of experimental and calculated density for R22 as a function of pressure

Figure 13 Comparaison des valeurs expérimentales et de la densité du R22 calculée en fonction de la pression

ation rises to 3.14%, with some very nearly critical points exceeding 40% error.

To illustrate the use of the general coefficients for the shape factors we performed two sets of density prediction calculations on R13b1. The data are from Jaeger⁵⁰ and Perelshtain and Aleshin⁶⁹. The pressure covered the range 0.4–10.4 MPa. The first set was made using the optimal coefficients for R13b1 as given in Tables 5 and 6. The results from this set of calculations are given in Figure 14 as shaded squares. The second set of computa-

tions was done using the general coefficients found in Equations (32) and (33). The deviations in predicted density for this case are given in Figure 14 as open squares. The average absolute deviation for the optimal coefficients is 0.95%, while for the general coefficients it is 1.63%. This is quite good considering that the only information required is the critical parameters, relative molecular mass and the acentric factor. Using the general coefficients, we could make predictions for any halocarbon refrigerant of interest.

Mixtures PVT results

We made comparisons of predicted volumes with experimental data for two binary refrigerant mixtures: R12/R114 and R22/R114. The data for these mixtures can be found in Ström⁶⁰, and cover several compositions in the compressed liquid region. Our model contains two binary interaction parameters k_{ij} and l_{ij} as shown in the combining rules, Equations (9) and (10). To find the interaction parameters we used a non-linear least squares fitting procedure with the objective function ψ defined in terms of volume:

$$\psi = \sum_{i=1}^n \left[\frac{(V_i^{\text{calc}} - V_i^{\text{exp}})}{V_i^{\text{exp}}} \right]^2 \quad (37)$$

We performed calculations with the interaction parameters set equal to 1, with optimal values found by fitting the data for both k_{ij} and l_{ij} , and with just the optimal k_{ij} found when l_{ij} was set to 1. The results are given in Table 8. The relative standard deviation in volume, σ_v , is here defined by

Table 7 Comparison of pure fluid density calculation with experimental data. (Density calculated using Equations (30), (31) and coefficients in Tables 5 and 6)

Tableau 7 Comparaison du calcul de la densité des fluides purs avec des données expérimentales (densité calculée avec les équations 30 et 31 et les coefficients de tableaux 5 et 6)

Fluid	Aad	Bias	RMS	N	Data source
R11	0.94	0.37	1.66	332	Benning and McHarness ⁵³ , Kremenevskaya and Rivkin ⁵⁴ , Altunin <i>et al.</i> ⁵⁵ , Chavez <i>et al.</i> ⁵⁶ , Kesselman <i>et al.</i> ¹⁴ , Rivkin and Kremenevskaya ¹⁴⁹ , Kremenevskaya and Rivkin ¹⁵⁰
R12	1.64	1.33	1.85	460	Bichowskii and Gilkey ⁶⁴ , Jaeger ⁵⁰ , Kumagai and Iwasaki ⁵⁸ , Takaishi <i>et al.</i> ⁵⁹ , McHarness <i>et al.</i> ⁶⁰ , Michels <i>et al.</i> ⁶² , Watanabe <i>et al.</i> ⁶³ , Castro-Gomez <i>et al.</i> ¹⁵¹ , Kells <i>et al.</i> ⁶⁰
R13	1.08	0.34	1.50	357	Albright and Martin ⁶⁵ , Shavandrin and Li ⁶⁸ , Oguchi <i>et al.</i> ⁶⁶ , Michels <i>et al.</i> ⁶² , Castro-Gomez <i>et al.</i> ¹⁵¹
R13b1	0.95	-0.43	1.60	93	Jaeger ⁵⁰ , Higashi <i>et al.</i> ⁷⁰ , Perelshtain and Aleshin ⁶⁹
R14	0.68	0.25	1.01	582	Shinsaka <i>et al.</i> ⁷⁵ , Knobler and Pings ⁷⁶ , Terry <i>et al.</i> ⁷⁷ , Tremaine and Robinson ⁷⁸ , Rubio <i>et al.</i> ¹⁵²
R22	0.59	0.29	1.35	616	Niesen <i>et al.</i> ³⁰ , Zander ⁸⁰ , Okada <i>et al.</i> ⁸⁴ , Kohlen <i>et al.</i> ⁸¹ , Higashi <i>et al.</i> ⁸⁵ , Kumagai and Iwasaki ⁵⁸ , Takaishi <i>et al.</i> ⁵⁹ , Benning and McHarness ⁵³ , Michels ¹⁵³
R23	1.00	0.11	1.78	591	Döring and Loeffler ⁹¹ , Hou and Martin ⁸⁷ , Shinsaka <i>et al.</i> ⁷⁵ , Shavandrin <i>et al.</i> ⁹² , Hori <i>et al.</i> ⁸⁸ , Wagner ⁸⁶ , Rubio <i>et al.</i> ¹⁵⁴
R32	1.90	-0.711	2.49	148	Malbrunot <i>et al.</i> ⁹³ , Kanungo <i>et al.</i> ⁹⁵ , Shinsaka <i>et al.</i> ⁷⁵ , Niesen <i>et al.</i> ⁹⁶
R113	1.04	0.74	1.82	212	Mastroianni <i>et al.</i> ⁹⁷ , Hovorka and Geiger ⁹⁹ , Benning and McHarness ⁵³ , Reidel ¹⁰⁰ , Geller ¹⁵⁵
R114	1.99	1.76	1.88	167	Wilson and Hules ¹⁰¹ , Martin ¹⁰² , Higashi <i>et al.</i> ¹⁰⁴ , Hasegawa <i>et al.</i> ¹⁰³
R115	1.98	1.37	2.12	81	Mears <i>et al.</i> ¹⁰⁵
R123	0.81	0.10	1.63	378	Schmidt ¹¹¹ , Morrison and Ward ²⁸ , Weber and Levelt Sengers ¹¹² , Oguchi and Takaishi ¹¹³ , Tanikawa <i>et al.</i> ¹¹⁴ , Maezawa <i>et al.</i> ²⁹ , Richard and Orfeo ¹¹⁵ , Fukushima <i>et al.</i> ²² , Weber ¹⁰⁷ , Fukushima ²¹ , Oguchi <i>et al.</i> ¹⁰⁹ , Piao <i>et al.</i> ¹¹⁰ , Baroncini <i>et al.</i> ¹⁵⁶
R124	0.93	0.75	1.05	154	Kubota <i>et al.</i> ¹¹⁶ , Shankland <i>et al.</i> ¹¹⁷ , Niesen <i>et al.</i> ³⁰
R125	0.85	0.58	0.90	180	Shankland <i>et al.</i> ¹¹⁸ , Wilson <i>et al.</i> ¹¹⁹ , Defibaugh and Morrison ¹²⁰
R134	0.74	-0.49	1.22	52	Ward and Morrison ¹²¹ , Maezawa <i>et al.</i> ¹²²
R141b	0.36	0.14	0.52	200	Morrison ¹²⁴ , Richard and Orfeo ¹²⁷ , Weber ¹²³ , Defibaugh <i>et al.</i> ¹²⁶ , Maezawa <i>et al.</i> ¹²²
R142b	1.85	0.12	3.55	315	Maezawa <i>et al.</i> ¹²⁸ , Mears <i>et al.</i> ¹²⁹ , Cherneeva ¹³⁰ , Valtz <i>et al.</i> ¹³² , Riedel ¹³¹ , Sousa <i>et al.</i> ¹⁵⁷ , Yada <i>et al.</i> ¹⁵⁸ , Takahashi <i>et al.</i> ¹⁵⁹
R143a	1.13	-0.51	1.59	32	Russell <i>et al.</i> ¹³³ , Mears <i>et al.</i> ¹²⁹ , Yokoyama and Takahashi ²³
R152a	1.44	-1.07	2.56	945	Sato <i>et al.</i> ¹³⁷ , Higashi <i>et al.</i> ¹³⁴ , Masui <i>et al.</i> ¹³⁸ , Mears <i>et al.</i> ¹²⁹ , Iso and Uematsu ¹³⁶ , Yada <i>et al.</i> ¹³⁵ , Blancke and Weiß ¹⁴⁰ , Geller <i>et al.</i> ¹⁴¹ , Tillner-Roth and Baehr ⁴¹ , Zhao <i>et al.</i> ¹³⁹ , Takahashi <i>et al.</i> ¹⁵⁹
R218	3.76	0.5	4.41	32	Brown ¹⁴²
RC270	0.64	0.24	0.93	77	Lin <i>et al.</i> ¹⁴³ , Lin <i>et al.</i> ¹⁴⁵

Table 8 Comparison of volume calculation with experimental data for binary refrigerant mixtures. (Volume calculated with Equations (30) and (31) with coefficients in Tables 5 and 6)

Tableau 8 Comparaison du volume calculé et des données expérimentales pour des mélanges binaires de frigorigènes (volume calculé avec les équations 30 et 31 et les coefficients des tableaux 5 et 6)

Mixture	k_{ij}	l_{ij}	σ_v
R12/R114	0.942	0.960	0.264
	0.991	1.000	0.497
	1.000	1.000	0.573
R22/R114	0.896	0.974	0.298
	0.930	1.000	0.348
	1.000	1.000	1.162

$$\sigma_v = \left[\sum_{i=1}^n \frac{[100(V_i^{\text{calc}} - V_i^{\text{exp}})/V_i^{\text{exp}}]^2}{(n-1)} \right]^{1/2} \quad (38)$$

The results for the R22/R114 and R12/R114 binary mixtures are good. Ström¹⁶⁰ calculated the relative standard deviation for these mixtures using three models: Thomson-Brobst-Hankinson (TBH), Lee-Kessler-Plocker (LKP), and Carnahan-Starling-deSantis (CSD). These models all contain only one binary interaction parameter. For the R12/R114 mixture, Ström¹⁶⁰ found relative standard deviations of 0.513, 0.540 and 0.861%

for the TBH, LKP and CSD models, respectively. For this mixture the new model has a relative standard deviation of 0.573 when interaction parameters are not used at all, of 0.497 when only one parameter is used and 0.264 when two interaction parameters are used. For the R22/R114 mixture Ström¹⁶⁰ found relative standard deviations of 0.379, 1.808 and 0.849% for the TBH, LKP and CSD models, respectively. We found the relative standard deviation to be 1.558 without any interaction parameters, 0.348 with one interaction parameter k_{ij} and 0.298 with both interaction parameters. The k_{ij} interaction parameter can be thought of as dealing with energy, while the l_{ij} parameter is more closely related to volume. The model is quite sensitive to the values of interaction parameter used, but with only the k_{ij} interaction parameter gives superior results to the TBH, LKP and CSD models for these two mixtures.

We have also made volume comparisons on ternary mixtures of R152a, R12 and R113 using data from Valtz *et al.*¹⁶¹. Several compositions at different temperatures at the bubble point are represented, a total of 16 points. The experimental bubble point pressure and temperatures were input and the saturated liquid volume was calculated. Three cases were examined: without interaction parameters, with an optimized k_{ij} , and with optimized k_{ij} and l_{ij} . The results, in terms of the relative standard deviation in volume, as well as the optimized

Table 9 Relative standard deviation for volume calculation of a R152a (1), R12 (2), R113 (3) ternary mixture

Tableau 9 Ecart relatif normal pour le calcul du volume d'un mélange ternaire à base de R152a (1), R12 (2) et R113 (3)

Pair	k_{ij}	l_{ij}	σ_v
1-2	1.000	1.000	2.241
1-3	1.000	1.000	
2-3	1.000	1.000	
1-2	1.012	1.000	0.557
1-3	0.983	1.000	
2-3	0.915	1.000	
1-2	0.880	0.929	0.386
1-3	1.082	1.064	
2-3	0.941	1.036	

values of the interaction parameters, are given in *Table 9*. Even without interaction parameters the predictions are within 3%. Dramatic improvement occurs with the use of interaction parameters, when the σ_v was reduced from 2.241 to 0.386.

Summary

We have developed a predictive corresponding states method for refrigerants using R134a as a reference fluid, incorporating recent coefficients for a 32-term MWBR equation of state for R134a. The model has been implemented in a computer program¹⁶². Shape factors for 21 refrigerants were found along the saturation boundary and fitted to a density-independent empirical correlation. Coefficients for shape factors for the 21 refrigerants are given, as well as a set of universal coefficients that can be used with any halocarbon refrigerant knowing only the critical parameters and the acentric factor. Results for density prediction for pure fluids are generally accurate to within a few percent. Volume predictions and interaction parameters for two binary and a ternary refrigerant mixture are given.

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