



# A perturbed hard sphere chain equation of state for applications to hydrofluorocarbons, hydrocarbons and their mixtures

Maurizio Fermeglia,<sup>\*,†</sup> Alberto Bertucco<sup>‡</sup> and Sonia Bruni<sup>‡</sup>

<sup>†</sup> Dipartimento di Ingegneria Chimica, Ambiente e Materie Prime Università di Trieste, Piazzale Europa 1, I-34127 Trieste, Italy

<sup>‡</sup> Istituto Impianti Chimici, Università di Padova, via Marzolo 9, I-35131 Padova, Italy

(Received 12 September 1997; accepted 21 March 1998)

**Abstract**—The evaluation of thermodynamic properties of pure hydrofluorocarbons and hydrocarbons, and their binary mixtures is considered. A modification of the *perturbed-hard-sphere-chain* equation of state is applied to these compounds and tested on a large database of refrigerants, hydrocarbons and their mixtures, with reference to both volumetric and equilibrium properties. The ability of the proposed model to reproduce experimental values is discussed. First, the theoretical background of the model is revisited in order to obtain a predictive method for the ‘a priori’ calculation of the values of parameters which reflect the size, shape and interaction energy of the molecule (three parameters for each pure component). Expressions to predict these values as a function of molecular quantities are presented and it is shown that the proposed model can be reliably used for calculating the properties of pure refrigerants and hydrocarbons, starting from the Bondi volume and surface area values, and the vapor pressure curve (2% error in the PVT behavior at worst). Then, the extension to mixtures is addressed. Attention is focused on the evaluation of binary interaction parameters ( $k_{ij}$ ) for systems of refrigerant–refrigerant, hydrocarbon–refrigerant and hydrocarbon–hydrocarbon type. Vapor–liquid equilibrium data of eighteen binary systems at several temperatures have been regressed, with errors in pressure ranging below 2% for refrigerant and below 1% for hydrocarbons when using a single value of  $k_{ij}$  for each binary pair, independent of temperature.  
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**Keywords:** Refrigerant; equation of state; perturbation theory; thermodynamics; binary mixtures.

## INTRODUCTION

In the engineering practice there is a strong and current need of an equation of state (EOS) suitable to represent both volumetric and equilibrium properties of new refrigerants, to be used as working fluids in existing and future refrigeration units in substitution of chlorinated and fluorochlorinated compounds. Since no existing pure fluids are able to ensure as high performances as those provided by the ones to be phased out, any proposed model must be able to calculate accurately mixture properties as well as pure component ones, possibly within a predictive framework. It would be also desirable that the model could account for the change of refrigerant properties due to interactions with lubricant oils, which are often present in refrigeration cycles, since even small

amounts of oil may have remarkable effects on the thermodynamic behavior of refrigerants, such as modifying the equilibrium pressure or inducing a liquid–liquid phase splitting. Therefore, the equation of state should account for the presence of long-chain molecules and provide the possibility of representing also liquid–liquid equilibria (LLE). The poor volumetric behavior of the cubic equations of state and their inherent difficulty of describing LLE was already discussed in a previous paper (Fermeglia *et al.*, 1997) in which models based on perturbation theories have shown to be more reliable due to their theoretically correct development.

The present paper is a contribution to the development of a model based on the perturbed hard-sphere-chain theory (PHSCT) (Song *et al.*, 1994a) for the description of refrigerant mixtures, with the same ultimate goal summarized in our previous work, dedicated to pure refrigerants (Fermeglia *et al.*, 1997).

\* Corresponding author.

In the literature it is shown how the PH SCT EOS can correlate with good accuracy and predict with sufficient precision the behavior of long-chain pure-component properties as well as small molecules and is, for example, suitable for describing polymer-containing mixtures, with respect also to the liquid-liquid phase splitting problem (Song *et al.*, 1994b).

In a recent paper, a new and improved version of the PH SCT model was proposed (Song *et al.*, 1996), in which a scaling factor, whose theoretical meaning was doubtful, was removed to allow also a simpler extension of the model to mixtures. As a consequence, the new model requires the recalculation of the parameter values for pure components (refrigerants and hydrocarbons) as well as a careful check of the performance of the model for the pure components.

To this purpose, the paper focuses on this new version of the PH SCT EOS and aims at:

- recalculating the pure component properties of the refrigerants and hydrocarbons,
- showing that the PH SCT EOS can be applied with success to simulate the VLE behavior of binary mixtures of small molecules by using only one adjustable parameter per pair.

## THEORY

### Pure components

The equation of state considered in this work is based on the simplified PH SCT (Song *et al.*, 1996). According to this model, the molecule is considered being constituted by chains of freely jointed tangent hard spheres (or segments). The PH SCT EOS has been developed starting from the modified Chiew equation of state for hard-sphere chains as the reference term (Chiew, 1990), a van der Waals-type perturbation term and the Song-Mason (Song and Mason, 1991) method to relate equation of state parameters to the intermolecular potential. For a summary of the model, as developed for applications to refrigerant and hydrocarbons we refer to our previous paper (Fermeiglia *et al.*, 1997); here, only the major changes from the original version to the new one are described.

According to the PH SCT EOS, the Chiew expression for hard spheres has been taken as the reference term, while the simplest van der Waals attractive form is used for the perturbation term. The equation finally derived is:

$$\left(\frac{P}{\rho kT}\right) = 1 + r^2 b \rho g(d^+) - (r-1)[g(d^+) - 1] - \frac{r^2 a p}{kT} \quad (1)$$

where  $P$  is the pressure,  $T$  the absolute temperature,  $\rho = N/V$  the number density,  $N$  the number of molecules,  $V$  the volume of the system,  $k$  the Boltzmann's constant,  $d$  the hard-sphere diameter and  $g(d^+)$  the pair radial distribution function of hard spheres at contact (the symbol  $+$  indicates that the hard spheres

are at contact). Three parameters appear in eq. (1):  $r$  is the number of segments (hard spheres) per molecule,  $a$  reflects the attractive forces between two non-bonded segments and  $b$  is the Van der Waals covolume per segment. These three parameters have clear physical meaning: respectively, the number of effective hard spheres per molecule ( $r$ ), the intermolecular potential-well depth between a non-bonded pair of segments ( $a$ ) and the segmental diameter ( $b$ ).

To obtain an engineering-oriented equation of state, expressions for  $a$  and  $b$  in term of constants associated with intermolecular forces are needed. These have been obtained according to the method of Song and Mason (1991), who showed that  $b(T)$  and  $a(T)$  are insensitive to the detailed shape of the pair potential:

$$a(T) = \frac{2\pi}{3} \sigma^3 \varepsilon F_a(kT/\varepsilon) \quad (2)$$

$$b(T) = \frac{2\pi}{3} \sigma^3 F_b(kT/\varepsilon) \quad (3)$$

where  $\varepsilon$  and  $\sigma$  are pair-potential parameters:  $\varepsilon$  is the depth of the minimum in the pair potential and  $\sigma$  is the separation distance between segment centers at this minimum. In eqs. (2) and (3)  $F_a$  and  $F_b$  are universal function of the reduced temperature  $kT/\varepsilon$ . Originally, these two functions were determined from experimental data for argon and methane, for which it is assumed  $r = 1$  and, in order to apply them to molecular fluids ( $r > 1$ ), a parameter  $s$  had been introduced for re-scaling the two functions with respect to temperature. Song *et al.* (1996) have discussed that the evaluation of parameter  $s$  in mixtures is questionable and according to them leads to arbitrary combining rules for mixtures. Consequently, they proposed the simplified version of the PH SCT EOS, in which the scaling factor  $s$  is removed and  $F_a$  and  $F_b$  are determined from thermodynamic properties of argon and methane over large range of temperature and density: they are expressed by the empirical equations:

$$F_a(kT/\varepsilon) = \alpha_1 \exp[-\alpha_2(kT/\varepsilon)] + \alpha_3 \exp[-\alpha_4(kT/\varepsilon)^{3/2}] \quad (4)$$

$$F_b(kT/\varepsilon) = \beta_1 \exp[-\beta_2(kT/\varepsilon)^{1/2}] + \beta_3 \exp[-\beta_4(kT/\varepsilon)^{3/2}] \quad (5)$$

with  $\alpha_i$  and  $\beta_i$  being constants whose values are given in Table 1.

In summary, the simplified PH SCT EOS for simple fluids has two parameters:  $\sigma$  and  $\varepsilon/k$ . In the case of molecular fluids and chainlike molecules, the model needs a third parameter ( $r$ ) which represents the number of segments per molecule and accounts for molecular size.

According to literature's suggestions (Song *et al.*, 1991, Fermeiglia *et al.*, 1997) it is more convenient to redefine these parameters through quantities which reflect the size, shape and energetic interactions of the fluids considered. Accordingly, they have defined

Table 1. Numerical values of constants to be used in eqs (4) and (5)

Constant	Value
$\alpha_1$	1.8681
$\alpha_2$	0.0619
$\alpha_3$	0.6715
$\alpha_4$	1.7317
$\beta_1$	0.7303
$\beta_2$	0.1649
$\beta_3$	0.2697
$\beta_4$	2.3973

a characteristic volume,  $V^*$

$$V^* = (\pi/6) r \sigma^3 N_A \quad (6)$$

where  $N_A$  is Avogadro's constant; a characteristic surface area,  $A^*$ :

$$A^* = \pi r \sigma^2 N_A \quad (7)$$

and a characteristic 'cohesive' energy,

$$E^* = r(\epsilon/k) R_g \quad (8)$$

where  $R_g$  is the gas constant.

#### Mixtures

The extension to mixtures of the PHSCCT EOS is straightforward, and can be obtained by applying mixing rules to the EOS parameters discussed in the previous section, and this leads to the following equation (Song *et al.*, 1994b):

$$\frac{P}{\rho kT} = 1 + \rho \sum_{ij} x_i x_j r_i r_j b_{ij} g_{ij}(d_{ij}^+) - \sum_i x_i (r_i - 1) \times [g_{ii}(d_{ii}^+) - 1] - \frac{\rho}{kT} \sum_{ij} x_i x_j r_i r_j a_{ij} \quad (9)$$

where  $x_i = N_i/N$  is the number fraction of molecules,  $r_i$  the number of segments for the  $i$ th component and  $g_{ij}(d_{ij}^+)$  the  $ij$  pair radial distribution function of hard-sphere mixtures at contact. The exact statistical mechanic analytical expression for  $g_{ij}(d_{ij}^+)$  of Boublik–Mansoori–Carnahan–Starling (BMCS) (Boublik, 1970; Mansoori, *et al.*, 1971) has been used in the model:

$$g_{ij}(\eta, \xi_{ij}) = \frac{1}{1-\eta} + \frac{3}{2} \frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{ij}^2}{(1-\eta)} \quad (10)$$

where  $\eta$  is the packing fraction:

$$\eta = \frac{\rho}{4} \sum_i x_i r_i b_i \quad (11)$$

and  $\xi_{ij}$  is given by

$$\xi_{ij} = \left( \frac{b_i b_j}{b_{ij}} \right)^{1/3} \frac{\rho}{4} \sum_k x_k r_k b_k^{2/3}. \quad (12)$$

For each binary pair, two parameters  $a_{ij}$  and  $b_{ij}$  are needed:  $a_{ij}$  is the attractive forces parameter and  $b_{ij}$

is the second cross virial coefficient of hard-sphere mixtures. These parameters can be obtained by extensions of eqs (2) and (3):

$$a_{ij} = (2\pi/3) \sigma_{ij}^3 \epsilon_{ij} F_a (kT/\epsilon_{ij}) \quad (13)$$

$$b_{ij} = (2\pi/3) \sigma_{ij}^3 F_b (kT/\epsilon_{ij}) \quad (14)$$

where  $F_a$  and  $F_b$  are defined in eqs (4) and (5). The combining rule for  $\sigma$  is defined as a consequence of the additivity of the hard-sphere diameters without any interaction parameter, even if it is possible to include a binary interaction parameter in this combining rule to improve the flexibility of the model:

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2. \quad (15)$$

In this work one binary interaction parameter,  $k_{ij}$ , is introduced in the combining rule for the energetic parameter:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} (1 - k_{ij}). \quad (16)$$

It is interesting to notice that in the original version of the PHSCCT EOS the expressions of  $b_{ij}$  and  $a_{ij}$  were different, because of the presence of the scaling factor  $s$  and the impossibility to define a parameter  $s$  for mixtures:

$$a_{ij} = (2\pi/3) \sigma_{ij}^3 \epsilon_{ij} \sqrt{F_a \left( \frac{kT}{\epsilon_i s_i} \right) F_a \left( \frac{kT}{\epsilon_j s_j} \right)} \quad (17)$$

$$b_{ij} = (2\pi/3) \sigma_{ij}^3 \sqrt{F_b \left( \frac{kT}{\epsilon_i s_i} \right) F_b \left( \frac{kT}{\epsilon_j s_j} \right)} \quad (18)$$

It is useful to transform eq. (9) from *number basis* to *segment basis*:

$$\frac{P}{\rho_r kT} = 1 + \rho_r \sum_{ij} \phi_i \phi_j b_{ij} g_{ij}(d_{ij}^+) - \sum_i \phi_i \left( 1 - \frac{1}{\eta} \right) g_{ii}(d_{ii}^+) - \frac{\rho_r}{kT} \sum_{ij} \phi_i \phi_j a_{ij} \quad (19)$$

where

$$\rho_r = N_r/V \quad (20)$$

$$\phi_i = N_i r_i / N_r = x_i r_i / \sum_j x_j r_j \quad (21)$$

$$N_r = \sum_i^m N_i r_i. \quad (22)$$

Equations (1) and (19) are the PHSCCT written in terms of pressure. It is more convenient to express the model in terms of Helmholtz energy since analytical expressions for all the thermodynamic properties may be obtained in a modular and efficient way by partial differentiation of the Helmholtz energy surface with respect to either the number of moles or the temperature or the volume (Mollerup and Michelesen, 1992). This procedure has been used in this paper for developing the model and writing the thermodynamic subroutines of the computer programs used for the calculations.

The Helmholtz energy expression for mixtures is the following:

$$\begin{aligned} \frac{A}{N_r kT} &= \sum_{i=1}^m \frac{\phi_i}{r_i} \frac{A_i^0}{kTN_i} + \rho_r \sum_{i=1}^m \sum_{j=1}^m \phi_i \phi_j b_{ij} W_{ij} \\ &\quad - \sum_{i=1}^m \phi_i \left(1 - \frac{1}{r_i}\right) Q_{ii} \\ &\quad - \frac{\rho_r}{kT} \sum_{i=1}^m \sum_{j=1}^m \phi_i \phi_j a_{ij} + \sum_{i=1}^m \frac{\phi_i}{r_i} \ln \left( \rho_r kT \frac{\phi_i}{r_i} \right) \end{aligned} \quad (23)$$

with  $A^0$  the pure component ideal gas term and

$$\begin{aligned} W_{ij} &= W_{ij}(\eta, \xi_{ij}) = \frac{1}{\rho_r} \int_0^{\rho_r} g_{ij} d\rho_r \\ &= \frac{I_1}{\eta} + \frac{3}{2} \frac{\xi_{ij}}{\eta^2} I_2 + \frac{1}{2} \frac{\xi_{ij}^2}{\eta^3} I_3 \end{aligned} \quad (24)$$

$$\begin{aligned} Q_{ij} &= Q_{ij}(\eta, \xi_{ij}) = \int_0^{\rho_r} (g_{ij} - 1) \frac{d\rho_r}{\rho_r} \\ &= -\ln(1 - \eta) + \frac{3}{2} \frac{\xi_{ij}}{\eta^2} + \frac{1}{4} \frac{\xi_{ij}^2}{(1 - \eta)^2} \end{aligned} \quad (25)$$

$$\eta = \frac{\rho_r}{4} \sum_i \phi_i b_i \quad (26)$$

$$\xi_{ij} = \left( \frac{b_i b_j}{b_{ij}} \right)^{1/3} \frac{\rho_r}{4} \sum_k \phi_k b_k^{2/3} \quad (27)$$

$$I_n = -I_{n-1} + \frac{1}{n-1} \frac{\eta^{n-1}}{(1-\eta)^{n-1}}, \quad I_1 = -\ln(1-\eta). \quad (28)$$

The chemical potential for a component in the mixture is obtained by partial differentiation of the

residual Helmholtz energy with respect to the number of moles (Bruni, 1997):

$$\begin{aligned} \frac{\mu_k}{kT} &= \frac{\mu_k^0}{kT} + 2r_k \rho_r \sum_{i=1}^m \phi_i b_{ik} W_{ik} \\ &\quad + \sum_{i=1}^m \phi_i \phi_j b_{ij} \left( N_r \frac{\partial W_{ij}}{\partial N_k} \right) - (r_k - 1) Q_{kk} \\ &\quad - \sum_{i=1}^m \phi_i \left(1 - \frac{1}{r_i}\right) \left( N_r \frac{\partial Q_{ii}}{\partial N_k} \right) \\ &\quad - \frac{2r_k \rho_r}{kT} \sum_{i=1}^m \phi_i a_{ik} + \ln \left( \frac{\phi_k}{r_k} \rho_k kT \right). \end{aligned} \quad (29)$$

## CALCULATION METHODS

### Pure components

The data base of refrigerants and hydrocarbons for pure components calculations used in this work is exactly the same as that of a previous paper to which we refer for literature citation and range of temperature and pressure (Fermeleglia *et al.*, 1997). A number of long-chain hydrocarbons have been included in the database as representative of the structure of compounds used as lubricant oils. For each pure component a fit for determining the best parameters was performed with the following objective function:

$$\begin{aligned} \text{OF} &= w_1 \sum_i \frac{(P_i^{\text{y,EXP}} - P_i^{\text{y,CALC}})^2}{(P_i^{\text{y,EXP}})^2} \\ &\quad + w_2 \sum_i \frac{(v_{\text{Load},i}^{\text{EXP}} - v_{\text{Load},i}^{\text{CALC}})^2}{(v_{\text{Load},i}^{\text{EXP}})^2} \\ &\quad + w_3 \sum_i \frac{(\rho_i^{\text{EXP}} - \rho_i^{\text{CALC}})^2}{(\rho_i^{\text{EXP}})^2} \end{aligned} \quad (30)$$

Table 2. List of binary systems investigated

System	Reference	$T$ (K)
Propane– $n$ butane	Kay (1970)	353.15–363.15
Propane– $n$ pentane	Sage and Lacey (1940)	344.26–360.93
Propane– $n$ hexane	Kay (1948)	333.15–353.15
Propane– $n$ heptane	Kay (1971)	353.15
Propane– $n$ decane	Reamer and Sage (1966)	277.59–344.26
R22– $n$ hexane	Xu <i>et al.</i> (1991)	363.00
R134A–Propane	Kleiber (1994)	255.00–298.00
R13–R14	Kubik and Stein (1981)	199.82–222.04
R13–R23	Stein and Proust (1971)	199.79–244.77
R14–R23	Piacentini and Stein (1967)	145.15–199.82
R22–R23	Roth <i>et al.</i> (1992)	273.15–293.15
R22–R123	Kleiber (1994)	313.15–333.70
R22–R114	Kruse <i>et al.</i> (1989)	253.15–338.15
R22–R142B	Stroem <i>et al.</i> (1993)	263.15–293.15
R114–R113	Lee <i>et al.</i> (1988)	348.20–398.10
R134A–R23	Roth <i>et al.</i> (1992)	255.00–265.00
R134A–R142B	Kleiber (1994)	268.00–298.00
R134A–R152A	Kleiber (1994)	255.00–298.00

Table 3. Optimal value of the parameters and RSMD [eq. (31)] for vapor pressure and volumetric properties at saturation (VLE) and in the single-phase region (PVT)

Substance	Optimal values of parameters			Vapor pressure	RMSD	
	$A^*$ ( $10^{-9}$ cm <sup>2</sup> /mol)	$V^*$ (cm <sup>3</sup> /mol)	$E^*$ (bar dm <sup>3</sup> /mol)		Volume	
					VLE	PVT
<i>(a) Refrigerants</i>						
R22	6.033	33.54	44.480	1.77	2.09	2.48
R32	4.787	24.70	42.161	0.80	0.39	4.63
R123	9.182	54.53	63.089	2.98	4.74	1.65
R143A	6.710	38.70	42.994	2.32	3.65	2.74
R134A	6.782	41.40	45.086	1.35	0.39	2.09
R142B	7.950	44.56	52.682	0.98	2.03	2.98
R152A	6.468	35.29	49.721	1.39	1.87	1.08
R13	6.184	38.83	32.731	2.08	2.76	1.97
R14	5.303	30.97	24.562	2.41	2.62	2.22
R21	6.779	41.56	52.294	2.57	3.54	2.12
R23	5.218	26.83	36.784	2.59	1.88	2.04
R113	9.869	66.55	61.601	2.96	1.00	2.77
R114	9.206	59.81	53.061	1.71	3.18	1.42
R115	8.505	52.67	44.944	2.32	3.43	2.55
Average				2.02	2.61	2.34
<i>(b) Hydrocarbons</i>						
Ethane	4.979	31.83	29.562	1.85	1.76	
Propane	6.613	42.79	39.854	4.21	2.95	
<i>n</i> Butane	7.982	53.83	48.465	2.34	3.32	
<i>n</i> Pentane	9.685	63.74	60.076	3.19	4.79	
<i>n</i> Hexane	11.208	73.85	70.152	3.99	5.18	
<i>n</i> Heptane	12.706	83.87	79.969	3.58	5.47	
<i>n</i> Octane	14.050	94.34	87.701	4.71	5.92	
<i>n</i> Nonane	15.175	106.01	93.288	8.28	4.70	
<i>n</i> Decane	17.075	112.98	108.960	5.24	5.63	
<i>n</i> Undecane	18.718	121.41	121.520	4.74	6.27	
<i>n</i> Dodecane	20.121	131.19	130.510	6.19	6.07	
<i>n</i> Tridecane	21.339	144.45	133.888	8.34	4.98	
<i>n</i> Tetradecane	23.173	144.99	157.150	3.92	7.74	
<i>n</i> Pentadecane	25.059	155.15	170.560	3.43	7.03	
<i>n</i> Hexadecane	26.286	167.84	174.090	5.92	6.27	
<i>n</i> Heptadecane	28.269	169.09	199.850	4.87	8.26	
<i>n</i> Octadecane	286.32	181.71	193.160	5.49	7.93	
<i>n</i> Nonadecane	30.458	193.80	203.320	5.13	6.98	
<i>n</i> Eicosane	31.968	204.24	213.390	10.20	6.74	
Cyclopentane	7.956	54.85	57.418	1.52	4.35	
Cyclohexane	9.128	64.13	64.819	2.12	3.36	
Ethylene	4.598	28.68	26.955	1.53	1.58	
Propylene	6.187	39.22	38.835	3.03	2.33	
Benzene	8.083	53.31	66.100	1.73	3.13	
Toluene	9.704	64.81	75.265	3.08	3.78	
Ethylbenzene	11.133	75.11	83.433	3.74	4.22	
Propylbenzene	12.690	85.10	91.998	4.72	4.34	
Chlorobenzene	9.263	63.84	76.797	2.81	3.25	
Fluorobenzene	8.528	56.35	67.962	2.29	3.44	
Styrene	10.735	71.52	85.672	2.16	3.59	
Acetone	7.226	43.79	63.630	3.29	1.53	
Chloroform	7.593	47.06	64.489	2.54	3.91	
Butyl acetate	12.332	77.97	89.633	6.36	4.30	
Average				4.03	4.56	

Table 4. PH SCT linear correlation parameters

Expression	Refrigerants		Hydrocarbons	
	<i>m</i>	<i>q</i>	<i>m</i>	<i>q</i>
(a) <i>Refrigerants</i>				
$A^* = m A_{vdw} + q$	0.943	1.355	0.959	1.328
$V^* = m V_{vdw} + q$	0.869	2.781	0.670	13.504
$E^* = m E_{coh} + q$	2.777	-3.746	3.423	-23.667
(b) <i>Hydrocarbons</i>				
$A^* = m A_{vdw} + q$	0.665	2.037	0.788	1.866
$V^* = m V_{vdw} + q$	1.269	-1.619	1.249	-3.691

$A_{vdw}$  and  $V_{vdw}$  are the van der Waals area and volume calculated according to Bondi (1968) and  $E_{coh}$  is the cohesive energy (Fermeleglia *et al.*, 1997). Table 4(a) refers to the correlation of data of Table 3 while Table 4(b) to those of Table 5.

where the properties considered are the vapor pressure, the saturated liquid volume and single phase PVT data weighted according to  $w_i$ . The evaluation index for a generic property  $M$  which will be reported later with the results, is the root mean squared deviation (RMSD) defined as follows:

$$\text{RMSD} = 100 \sum_i \sqrt{\frac{(M_i^{\text{EXP}} - M_i^{\text{CALC}})^2}{\text{NDAT}(M_j^{\text{EXP}})^2}} \quad (31)$$

The algorithms for calculating the density and the pure component equilibrium are described elsewhere (Patrizio, 1995).

#### Mixtures

Only one binary interaction parameter ( $k_{ij}$ ) has been estimated by fitting binary vapor–liquid equilibrium (VLE) data. The systems investigated are summarized in Table 2 along with the literature references and the range of temperature. A parameter estimation program has been developed, with particular attention given to reducing the CPU time and to improve the reliability of the search procedure. The density calculation routine is based on the algorithm proposed by Topliss *et al.* (1988). For each data point, a bubble-point calculation at constant temperature has been performed at a given value of the binary interaction parameter. The following objective function was minimized:

$$\text{OF} = \sum_{i=1}^{\text{NP}} \left( \frac{P_i^{\text{CALC}} - P_i^{\text{EXP}}}{P_i^{\text{EXP}}} \right)^2 \quad (32)$$

where NP is the number of equilibrium data for a given system. The evaluation index for a generic property  $M$  is the same as for the case of the pure component properties. Details on equilibrium and density calculations are reported elsewhere (Bruni, 1997).

The results are presented in terms of per cent average deviations in pressure and mole fractions.

Relative pressure deviations are defined as:

$$\Delta P = \frac{100}{n} \sum_i \left| \frac{P_i^{\text{EXP}} - P_i^{\text{CAL}}}{P_i^{\text{EXP}}} \right| \quad (33)$$

To avoid unrealistic weighing of results in the dilute regions, the mole fractions deviations have been defined in absolute terms as follows:

$$\Delta y = \frac{1}{n} \sum_i |y_i^{\text{EXP}} - y_i^{\text{CAL}}| \quad (34)$$

Data regression with other objective functions have also been performed on selected binary systems, but no substantial difference has been observed in the parameters and statistical results; this is not surprising since high pressure equilibrium is most sensitive to pressure than to mole fraction variations even if appropriate weights are assigned to the terms of the objective function.

The convergence algorithm used to minimize the objective function of both pure components and mixtures is that of Levenberg–Marquardt in the modification of the IMSL routine ZXSSQ.

## RESULTS

#### Pure components

The data reduction results obtained by using the new version of the PH SCT EOS are summarized in Table 3 for refrigerants (3a) and hydrocarbons (3b). The values in Table 3 show that the simplified PH SCT EOS provides a satisfactory data fitting, especially when one considers that the expected experimental error in the measurements is around 1–2%. Furthermore, if compared with the previous version of the PH SCT, the results are very similar, although the original model performs slightly better. This allows us to conclude that the simplified version has the same capabilities of the original model as far as data regression is concerned for the compounds

Table 5. Results obtained by fitting volumetric data with the vapor pressure constrained to the experimental value

Substance	Optimal values of parameters		RMSD	
	$A^*$ ( $10^{-9}$ cm <sup>2</sup> /mol)	$V^*$ (cm <sup>3</sup> /mol)	Volume	
			VLE	PVT
<i>(a) Refrigerants</i>				
R22	5.038	36.554	0.43	2.47
R32	4.543	25.415	0.35	4.76
R123	7.096	62.867	0.50	
R134A	5.212	42.287	0.43	3.55
R143A	5.899	43.832	0.17	3.43
R142B	6.654	49.244	0.37	2.20
R152A	5.452	38.943	0.14	1.17
R13	5.321	40.124	0.78	0.98
R14	4.496	31.951	0.70	1.21
R21	5.642	43.484	0.76	0.98
R23	4.796	28.072	1.17	2.17
R113	7.740	72.326	0.58	0.72
R114	7.483	65.427	0.48	1.55
R115	6.615	57.951	0.39	1.37
Average			0.52	2.04
<i>(b) Hydrocarbons</i>				
Ethane	4.669	32.08	1.22	
Propane	6.062	43.63	1.68	
Butane	6.999	55.77	1.42	
Pentane	8.171	67.73	1.50	
Hexane	9.321	80.06	1.21	
Heptane	10.481	92.15	1.40	
Octane	11.184	105.84	1.06	
Nonane	12.346	118.36	1.24	
Decane	13.544	131.65	1.08	
Undecane	14.824	143.70	1.39	
Dodecane	15.898	156.93	1.31	
Tridecane	17.463	169.23	1.40	
Tetradecane	17.387	183.04	1.32	
Pentadecane	19.515	196.30	1.37	
Hexadecane	20.686	209.91	1.33	
Heptadecane	21.489	222.77	1.21	
Octadecane	21.038	237.82	0.96	
Nonadecane	23.642	249.08	1.30	
Eicosane	24.316	266.00	1.17	
Cyclopentane	6.137	56.82	0.74	
Cyclohexane	7.514	68.50	0.62	
Ethylene	4.316	28.93	0.98	
Propylene	5.818	39.74	1.75	
Benzene	6.819	56.72	0.59	
Toluene	8.496	67.98	1.52	
Ethylbenzene	9.662	79.51	1.62	
Propylbenzene	11.090	91.46	1.79	
Chlorobenzene	8.073	66.82	1.18	
Fluorobenzene	7.267	59.58	0.97	
Styrene	9.391	76.40	1.06	
Acetone	6.805	44.86	1.11	
Chloroform	6.461	49.78	1.02	
Butyl acetate	10.523	85.45	1.56	
Average			1.22	

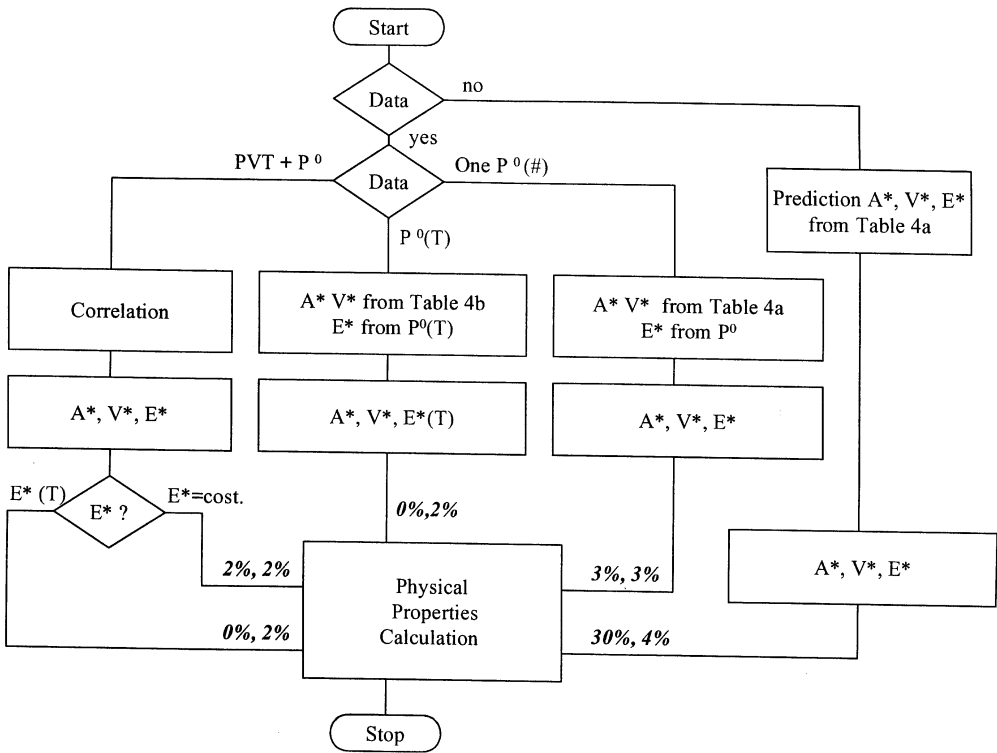


Fig. 1. Decision making chart for simplified PHSCCT pure component properties calculation: the deviations reported refers to vapor pressure (the first value) and to volumetric properties (the second value); the method indicated by # is described in Fermeiglia *et al.* (1997).

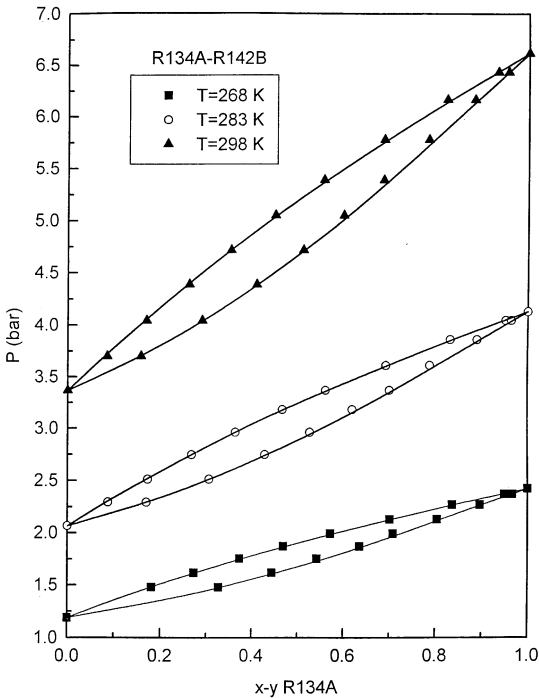


Fig. 2. VLE fitting of the R134A–R142B system at different temperatures.

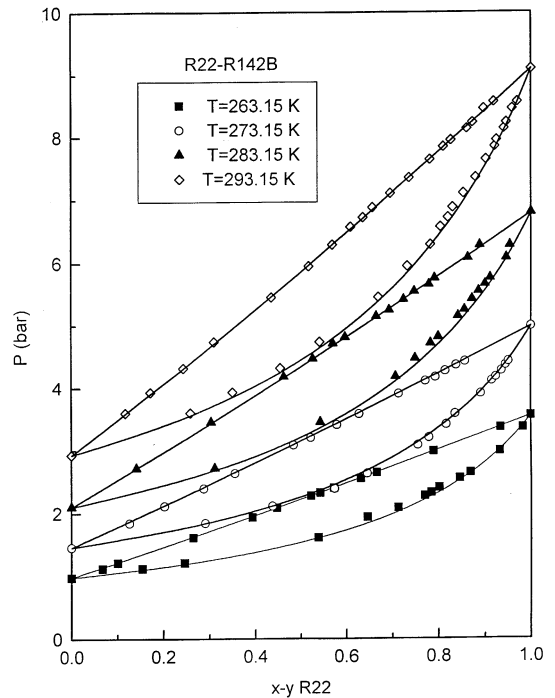


Fig. 3. VLE fitting of the R22–R142B system at different temperatures.



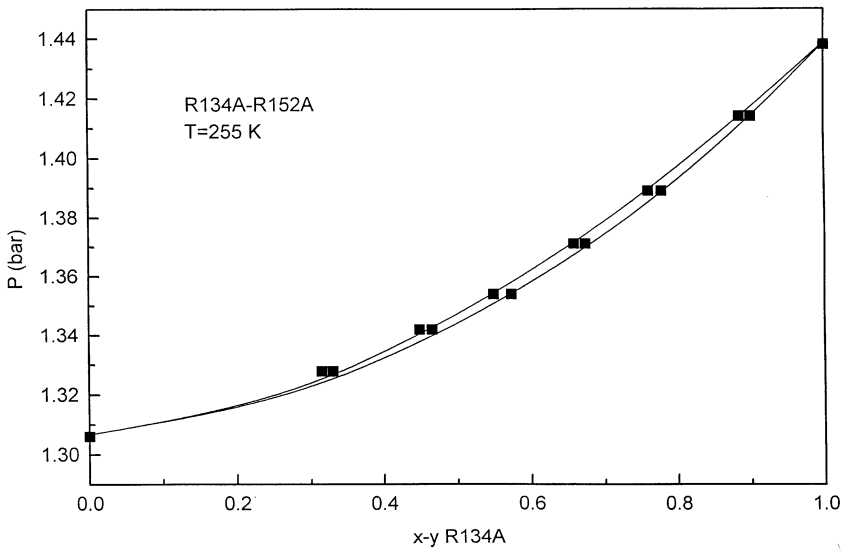


Fig. 4. VLE fitting of the R134A–R152A system at 255 K.

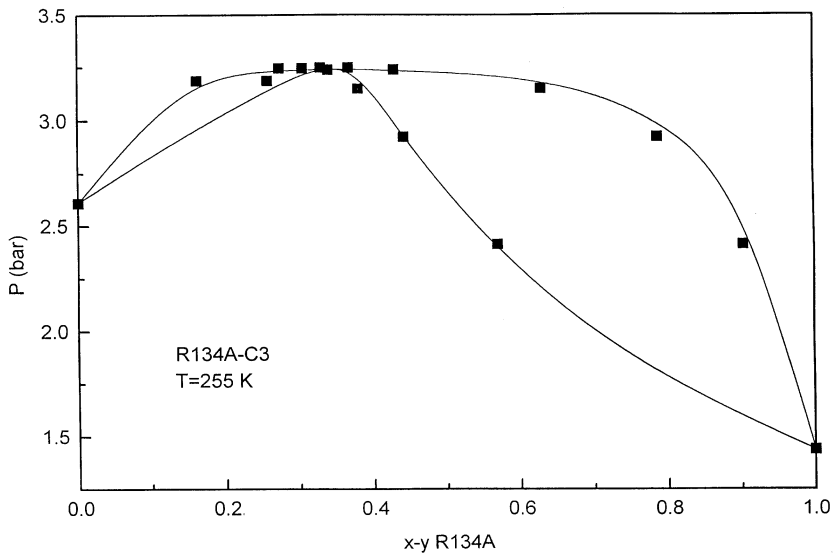


Fig. 5. VLE fitting of the R134A–Propane system at 255 K.

investigated. A comparison with the results obtained for the original model on the same database shows that, as expected, the numerical values of the parameters have changed.

As it was observed for the original model and for other models based on perturbation theories, the physical significance of the adjustable parameters allows correlating them with the molecular structure.

The procedure outlined in Fermeglia *et al.* (1977) has been adopted here for developing expressions for the  $A^*$  and  $V^*$  parameters as a function of the van der Waals area and volume (Bruni, 1997). Table 4(a) summarizes the linear correlation parameters recalculated based on the results presented in Table 3. The expres-

sions reported in Table 4(a) make the PHSCCT model fully predictive. In the previous paper, it has been shown that if one knows the vapor pressure curve the performance of the model can be substantially improved. To this end, volumetric (PVT and saturated liquid volume) data have been regressed and the  $A^*$  and  $V^*$  parameters have been calculated by constraining the calculated vapor pressure to be equal to the experimental values in the entire range of temperature considered. The results are reported in Table 5 and are very satisfactory especially for hydrocarbons. We note the improvement with respect to the results reported in Table 3 and to those obtained for the original model in which the average deviations on the same data base were 2.81 for VLE

Table 6. Deviations between calculated and experimental data for refrigerant–refrigerant systems: comparison between global and individual fitting

System	$T$ (K)	Individual fitting			Global fitting		
		$k_{ij}$	$\Delta P$	$\Delta y$	$k_{ij}$	$\Delta P$	$\Delta y$
R13–R14	199.82	0.0221	0.72	0.011	0.0183	1.02	0.014
	222.04	0.0146	0.84	0.012	0.0183	1.12	0.012
R13–R23	199.79	0.0700	1.48	0.013	0.0710	1.62	0.014
	244.77	0.0720	1.15	0.016	0.0710	1.11	0.016
R14–R23	145.15	0.0552	7.61	0.008	0.0570	7.93	0.009
	172.04	0.0592	4.22	0.010	0.0570	4.38	0.008
	199.82	0.0566	3.04	0.103	0.0570	3.08	0.103
R22–R23	273.15	0.0208	0.28	0.011	0.0166	0.95	0.011
	293.15	0.0123	0.67	0.016	0.0166	0.95	0.016
R22–R123	313.48	0.0189	1.30	0.012	0.0211	1.38	0.011
	333.70	0.0232	1.69	0.017	0.0211	1.92	0.017
R22–R114	253.15	0.0521	1.74	0.010	0.0572	2.35	0.016
	283.15	0.0547	0.91	0.023	0.0572	1.40	0.025
	313.15	0.0585	1.02	0.014	0.0572	0.98	0.014
	338.15	0.0635	0.91	0.019	0.0572	1.36	0.017
R22–R142B	263.15	0.0027	0.29	0.019	0.0044	0.59	0.021
	273.15	0.0023	0.26	0.008	0.0044	0.67	0.008
	283.15	0.0076	0.61	0.017	0.0044	0.31	0.012
	293.15	0.0049	0.23	0.009	0.0044	0.25	0.009
R114–R113	348.20	0.0027	0.28	—	– 0.0013	0.82	—
	373.10	– 0.0013	0.09	—	– 0.0013	0.09	—
	398.10	– 0.0054	0.40	—	– 0.0013	0.71	—
R134A–R23	255.00	0.0095	0.46	0.006	0.0090	0.46	0.006
	265.00	0.0086	0.50	0.009	0.0090	0.50	0.010
R134A–R142B	268.00	0.0144	0.14	0.007	0.0140	0.22	0.007
	283.00	0.0137	0.18	0.007	0.0140	0.19	0.007
R134A–R152A	298.00	0.0137	0.27	0.005	0.0140	0.27	0.005
	255.00	– 0.0052	0.07	0.044	– 0.0050	0.07	0.004
	275.00	– 0.0052	0.06	0.004	– 0.0050	0.06	0.004
	298.00	– 0.0054	0.06	0.004	– 0.0050	0.06	0.004
Average			1.05	0.014		1.23	0.015

Table 7. Deviations between calculated and experimental data for hydrocarbon–hydrocarbon systems: comparison between global and individual fitting

System	$T$ (K)	Individual fitting			Global fitting		
		$k_{ij}$	$\Delta P$	$\Delta y$	$k_{ij}$	$\Delta P$	$\Delta y$
Propane– <i>n</i> butane	353.15	0.0014	0.07	0.006	0.013	1.03	0.008
	363.15	– 0.0011	0.10	0.007	0.013	1.52	0.006
Propane– <i>n</i> pentane	344.26	0.0157	0.17	0.011	0.013	0.75	0.009
	360.93	0.0174	0.39	0.013	0.013	0.91	0.011
Propane– <i>n</i> hexane	333.15	– 0.0051	0.26	0.001	0.013	0.54	0.0002
	353.15	– 0.0009	0.10	0.002	0.013	1.22	0.001
Propane– <i>n</i> heptane	353.15	0.0076	0.08	0.006	0.013	0.27	0.006
Propane– <i>n</i> decane	277.59	0.0436	1.44	0.0002	0.013	12.63	0.0002
	310.93	0.0431	2.18	0.010	0.013	9.69	0.007
	344.26	0.0437	1.49	0.003	0.013	12.06	0.002
Average			0.63	0.006		4.06	0.005

and 2.78 for PVT of refrigerants. The new values of  $A^*$  and  $V^*$  have been used to calculate linear expressions which are reported in Table 4(b). With these values of parameters, the PHSC model can be extended to

components not originally included in the database provided their vapor pressure is known at the temperature of interest, in order to evaluate the energetic parameter.

Table 8. Deviations between calculated and experimental data for refrigerant–hydrocarbon systems: comparison between global and individual fitting

System	$T$ (K)	Individual fitting			Global fitting		
		$k_{ij}$	$\Delta P$	$\Delta y$	$k_{ij}$	$\Delta P$	$\Delta y$
R22– $n$ hexane	363.00	0.0607	0.97	0.013	0.0607	0.97	0.013
R134A–propane	255.00	0.1110	0.85	0.012	0.1130	0.89	0.015
	275.00	0.1140	0.87	0.013	0.1130	0.76	0.012
	298.00	0.1135	0.92	0.012	0.1130	0.93	0.011
Average			0.90	0.013		0.89	0.013

Table 9. Sensitivity of the pressure deviation to the binary interaction parameter  $k_{ij}$ 

System	$dP/dk$ (bar)	System	$dP/dk$ (bar)
R13–R14	0.79	Propane– $n$ butane	1.01
R13–R23	1.40	Propane– $n$ pentane	2.15
R14–R23	1.78	Propane– $n$ hexane	0.81
R22–R23	1.60	Propane– $n$ heptane	0.35
R22–R123	1.10	Propane– $n$ decane	3.66
R22–R114	1.20	R134A–propane	1.10
R22–R142B	1.76		
R114–R113	1.35		
R134A–R142B	2.00		

Figure 1 reports a decision making chart for the calculation of thermodynamic properties of pure components with an indication of the expected accuracy that one may achieve in the various cases.

### Mixtures

The pure component parameters in all the mixture calculation reported have been calculated according to the linear relationships of Table 4(b) and by using the vapor pressure data at the system temperature. For each binary system at a given temperature, the optimum interaction parameter  $k_{ij}$  has been determined from the experimental data of Table 2. Some results of binary VLE data correlation are depicted in Figs 2–5. The deviations [eqs (33) and (34)] and the numerical value of the  $k_{ij}$  parameters are presented in Tables 6–8 in which the global fitting over the entire temperature range is compared, for each system, with the one obtained at individual temperature.

Table 6 reports the values of the  $k_{ij}$  for the mixtures of refrigerants. In this case, it is evident that a single value of  $k_{ij}$  with no temperature dependence for each system is able to reproduce the data with accuracy as low as the experimental uncertainty.

Table 7 shows data for hydrocarbon–hydrocarbon mixtures. In this case a single value of the interaction parameter ( $k_{ij} = 0.013$ ) can be easily identified to describe the interactions between the hydrocarbon sites in an hydrocarbon mixture, thus making the model fully predictive. As far as the hydrocarbon–refrigerant systems are concerned, only few data have been con-

sidered (Table 8), since we have decided to restrict this investigation to data at temperature for which both components were sub-critical. This has limited the database of components, but allowed us a more precise determination of the pure component parameters. No trends or general value of the  $k_{ij}$  parameters can be observed with such a small number of systems, except that the  $k_{ij}$  can be considered constant within the temperature range considered.

Finally, since a good fit to the experimental data is not sufficient to conclude that the parameters are well estimated, in Table 9 the sensitivity of the pressure deviation [see eq. (33)] with respect to the binary interaction parameter is reported ( $\partial\Delta P/\partial k$ ) for some selected representative systems. These results show that the output is sensitive to the parameters and this allows us to conclude that, under the hypothesis of sufficiently accurate measurements, the parameter estimation procedure is correct.

Pure component vapor pressure and saturated volume is also very sensitive to the parameter values (Bruni, 1997).

### CONCLUSIONS

The simplified PHSCT model has been applied to pure refrigerants and hydrocarbons and their mixtures of possible industrial use. The simplified PHSCT model has shown the same good capability of the original model for the prediction of thermodynamic properties of pure refrigerant and hydrocarbons. By

using expressions of Table 4(b) and vapor pressure data, it is possible to achieve a precision comparable to the experimental error. A decision making chart has been reported to summarize the calculation procedure and the accuracy that one may expect by using the methods proposed in this work.

For binary mixtures, excellent results could be obtained with one single value of the  $k_{ij}$  interaction parameter, which is system dependent and not temperature dependent for the refrigerant–refrigerant and the refrigerant–hydrocarbon systems. The hydrocarbon–hydrocarbon systems are described satisfactorily by a single universal value of the  $k_{ij} = 0.013$ . The calculations reported in this work are very promising in view of the application of the model to multicomponent mixtures of refrigerants and hydrocarbons.

#### Acknowledgements

The authors thank N. Elvassore for helpful discussions and J.M. Prausnitz for fruitful suggestions. The Ministero dell'Università e della Ricerca Scientifica (MURST-Roma) is gratefully acknowledged for the financial support.

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