

Prediction of Thermodynamic Properties of the Systems Formed by *n*-Alkanes, Aliphatic Monoethers, and 1-Chloroalkanes, Using a Cell–Hole Group Contribution Model

Tadeusz Hofman

*Division of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology,
ul. Noakowskiego 3, 00-664 Warszawa, Poland*

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This work presents a comprehensive test of the group-contribution hole models used to predict thermodynamic properties of pure *n*-alkanes, aliphatic monoethers, 1-chloroalkanes and their mixtures with an *n*-alkane, which is based on numerous data of the following properties: P – ρ – T for liquids and gases, enthalpies of vaporization, saturated vapor pressures, excess enthalpies, excess volumes, infinite dilution activity coefficients, vapor-pressure equilibria under low and high pressure, and solid–liquid equilibria. It has been observed that a lattice–hole model does not provide a good description of the high-pressure liquid densities. A new predictive group-contribution cell–hole model is proposed to overcome this shortcoming. It incorporates the free volume contribution in the form deprived of the inconsistency found in the methods published earlier. Good accuracy of the prediction, better than that for the standard models, is confirmed.

1. Introduction

There exist numerous group-contribution models used to predict thermodynamic properties. They differ as to the theoretical rigor and the range of applicability. Usually the more theoretically justified model the more properties and the parameters it can describe. The UNIFAC model in its the most refined form,¹ which may be recognized as the most widespread group-contribution method of this kind, is able to predict the low-pressure mixture properties only, i.e., fluid-phase equilibria and mixing functions, excluding the excess volumes. More elaborated models, based on an equation of state, increase the number of properties they can deal with. Formally, all the configurational properties, concerning both pure compounds and mixtures should be described and predicted if the most elaborated form of a model is applied.

The majority of such methods are based on the lattice theory or employ some elements of it. Although this theory may be considered as out-dated now, still nothing more general has been proposed as far as the predictive methods are concerned. The models based on the distribution functions, which are more justified theoretically, as the SAFT model,^{2,3} hardly can be transformed in a consistent way into the group-contribution version what seems to be a necessary condition of any successful predictive model.

The development of the group-contribution lattice models has a long history. The first successful and widely applied model was that of UNIFAC.⁴ As based on the rigid-lattice simplification and the semiempirical excess Gibbs energy model, it is able to describe only the low-pressure vapor–liquid equilibria for mixtures. Some more refined modifications, mainly including multiparameter temperature dependencies, extend this set by the excess enthalpies yet.¹ These models, despite their simplicity and lack of the theoretical rigor, are used frequently and can be considered as the standards as long as the above-mentioned properties are concerned.

In 1974, the first group contribution equation of state was published.⁵ This method, known as that of Nitta and Chao, is based on the cell model and apart from the properties described

by the UNIFAC model, is able to deal with some pure compound and the volumetric properties. However, the equation of state it uses is applicable to the liquids only and hence the vapor properties and the high-pressure vapor–liquid equilibria escape from a possible description. Nevertheless, its limits of applicability exceed greatly these of the UNIFAC and the modified UNIFAC methods.

The Nitta–Chao method is neither more complicated numerically than the less advanced UNIFAC model nor less accurate, but only the latter point is being frequently applied if low-pressure mixture properties are to be predicted. This is mainly because of the large set of model parameters which are being continuously updated. Also computational programs of the UNIFAC models are easily available.

The further development of the group-contribution methods proceeded through the generalization of the lattice theory to describe the gas and vapor properties and the high-pressure vapor–liquid equilibria as well. Such an extension is possible if the existence of empty or vacant lattice knots is allowed. They are usually termed as “holes”. Hole models based on this idea are the most general and are able to describe all the configurational properties. In the last 3 decades, a few group-contribution hole models and their numerous versions have appeared.^{6–10} It may seem that their advantages and disadvantages should be clearly recognized. But it is not so. In fact abilities of these models are not well understood because of at least three reasons: (i) no extensive comparison of accuracies of these methods including a large number of data, systems and properties, has been ever published; (ii) no detailed discussion of some essential assumptions has been performed; (iii) no universal measure of accuracy has been applied to make possible such a comparison between results of various authors.

The first question set in this paper is following: what is the value of the existing predictive group-contribution hole models? May they be refined or improved to achieve a greater accuracy? As the answer turned out to be only partly positive for the first question and rather positive for the second one, a significant

modification of the model is proposed which removes the observed deficiencies.

2. The Hole Models

Any thermodynamic theory of the matter which counts possible states placing molecules or their parts (groups, segments) in the repeating units of space (the knots) is called the lattice theory. The main distinction concerns the character of knots. A molecule placed therein can be fixed or can move inside a certain restricted space limited by surrounding molecules. The latter case, which is more general, corresponds to the cell model; the former one is usually also termed as a lattice theory. Thus, the term "lattice model" or "lattice theory" possesses double meaning—it can be restricted to models based on the "molecule fixed in a lattice knot" assumption, but it can also include the cell models, as they apply the idea of a latticelike structure of the system.

To avoid an ambiguity, in this work the term "lattice theory" will be used in a narrower sense, while lattice models and cell models jointly will be described as "cell–lattice theories" or models. The cell theory, being more general, will be presented and discussed below. Lattice models will be interpreted as its special case.

In 1934 a fully elaborated cell theory of the fluid state was published by Lennard-Jones and Devonshire.¹¹ At the same time Eyring¹² suggested leaving some lattice knots vacant, thus initializing development of the hole theories. The first qualitatively derived hole model was that of Cernuschi and Eyring.¹³ The first models were applied to globular molecules only. Simultaneously considerable progress was noted in the description of chain molecules in the framework of the lattice theory.^{14–17} The results, originally applied to the rigid lattice models, found application in the cell models, too.

In the next 2 decades the hole models became popular and were extensively studied. A new idea was to calculate the equilibrium configuration including the cell volume, by the minimization of the system free energy.¹⁸ It has seemed, however, that in the late 1950s it became widely recognized that the hole theory did not fulfill the hopes which had been previously put into it. It was Barker¹⁹ who expressed this view openly in his monograph.

Almost simultaneously, a new impetus appeared. It was due to Henderson,²⁰ who got very good results with his hole model, thanks to small modifications of the free volume term. Henderson's paper practically finished the discussion and controversy on the hole models. It has gained acceptance while shortcomings have been realized. Later on numerous practical applications of the cell–lattice models were derived and used.^{6–10,21–31} Some of them were developed in the group-contribution version.^{6–10} A detailed derivation of the cell theory can be found in numerous monographs.^{19,32,33} Here only the final form and the most important conclusions will be presented.

The most general form of the configurational partition function for the cell model is the following one:

$$Q = g \left(\prod_i v_{fi}^{N_i} \right) \exp(-E_0/kT) \quad (1)$$

and the multiplication is performed over all molecules, N_i is the number of molecules of the i th component, g is the degeneracy factor (the combinatorial contribution), E_0 stands for the lattice energy and v_{fi} is the free volume. The free volume reduces itself to the space accessible for a molecule for the hard-sphere or the square-well potentials. The partition function (eq

1) is calculated for the equilibrium state, which corresponds to the most probable configuration of the molecules. In the most rigorous approach, it is derived through the maximization of the partition function.

Hence the configurational partition function for any cell model is a product of the three contributions—combinatorial, free volume, and the lattice energy. The detailed forms of these terms depend on a particular model.

3. Test of a Group-Contribution Hole Model

As it is not clear what is an accuracy of the group-contribution hole models, a comprehensive test of these methods is worth performing. To make such a test, at least five groups of problems must be resolved. They are as follows:

- (i) Selection of a sufficiently representative model.
- (ii) Minimization of the number of its parameters which minimizes the correlational character of a method.
- (iii) A precise definition of the parameter determination procedure, which must be the same for all the models being compared.
- (iv) Selection of a sufficiently large data set to be predicted—concerning both the number of systems and ranges of parameters as well as their variety.
- (v) Definition of an appropriate measure of the model accuracy.

The main controversy concerns the importance of the free volume term. In fact, majority of these models neglect this contribution,^{7,8,10} although without doubt there is sufficient room for a molecule (group, segment) to move inside its cell. It is not clear whether this factor is important if macroscopic properties are concerned. Hence, it would be desirable to test rather a lattice model. If some deficiencies appeared, they could be attributed to this simplification and eventually removed through incorporating of the free volume term. Usually the models applied in practice are developed in the forms having some empirical relationships, which are employed merely to ensure a sufficient flexibility. For example, the interaction energies are frequently expressed as an empirical function of temperature. If such assumptions appear it makes the model abilities difficult to interpret. In the case of an eventual success or a failure of a model, it is impossible to say whether it results from the model theoretical foundations or these additional empirical dependencies. Hence, it is important to discuss a model in its core form, deprived of such empirical dressings.

The Smirnova–Victorov model⁷ was selected as a representative of the lattice–hole models. It has been extensively applied in the group-contribution version for many kind of substances and properties, although mainly oriented on the high-pressure vapor–liquid equilibria.^{34–37} It was considerably simplified through neglect of the temperature dependence of the group interchange energies. It was shown that its simplified form gives even better prediction accuracy if a large amount of compounds and properties and a wide range of parameters are considered.³⁸

The equation of state for the Smirnova–Victorov model for the chainlike molecules is given by

$$p\omega/kT = -\ln\left(1 - \frac{1}{\bar{V}}\right) + \frac{z}{2}\ln\left(1 - \frac{1}{\bar{V}} + \frac{q_m}{\bar{V}r_m}\right) - z \ln X_0 \quad (2)$$

where ω is a cell volume, the reduced volume is defined as a ratio of the system volume to the volume of the occupied segments, i.e., $\bar{V} = V/\omega r_m$, z is the coordination number, r_m and q_m denote molar values of the number of segments and the number of external contacts; x_i is the mole fraction, and the

TABLE 1: The Model Parameters Which Must Be Adjusted for the Smirnova–Victorov^{7,38} and the Cell–Hole Group-Contribution Methods: Structural (S); Energetic (E); Those for Alkanes (A, CH₃,CH₂) and Those for a New Group Attached to an Aliphatic Chain (X)

model	no. of parameters ^a		description of parameters
	S	E	
Smirnova–Victorov simplified ³⁸	A	2	3 S, no. of segments (r_{CH_3}), cell vol (ω); (r_{CH_2} was assumed to equal 1) E, energy interactions between (CH ₃ –CH ₃), (CH ₂ –CH ₂), and (CH ₃ –CH ₂) contact sites
	X	1	2 S, no. of segments (r_{X}) E, energy interactions between (X–X) and (X–[CH ₂ ,CH ₃])
Smirnova–Victorov original ⁷	A	3	9 S, no. of segments (r_{CH_3}) and (r_{CH_2}), cell vol (ω) E, energy interactions between (CH ₃ –CH ₃), (CH ₂ –CH ₂) and (CH ₃ –CH ₂) contact sites ^b
	X	1	6 S, no. of segments (r_{X}) E, energy interactions between (X–X) and (X–[CH ₂ ,CH ₃]), (3 params)
cell–hole	A	3	3 S, hard core vols $v_{\text{CH}_3}^*$, $v_{\text{CH}_2}^*$, and chain flexibility factor c E, energy interactions between (CH ₃ –CH ₃), (CH ₂ –CH ₂), and (CH ₃ –CH ₂) contact sites
	X	1	2 S, hard core vol v_{X}^* E, energy interactions between (X–X), (X–[CH ₂ ,CH ₃])

^a Number of parameters to be adjusted for a group or a few groups. ^b Three parameters per each contact.

parameter X_0 is an element of the vector of auxiliary variables which pertains to the holes. The whole vector is a solution of the so-called quasichemical equations.^{7,39}

Table 1 gives a list of the model parameters for the both versions of the Smirnova–Victorov model^{7,38} which have to be determined through the adjustment to the experimental data. The cell–hole model, which will be presented later, is also described. The Smirnova–Victorov model in its simplified form requires a considerably lower number of its parameters despite the same extent of an applicability. It is also lower than for the less general modified UNIFAC¹ and the Nitta–Chao⁵ models.

It was assumed that the energies of interactions between an optional group X and both aliphatic groups (–CH₃, –CH₂) are related to the energies of the interaction between like aliphatic ones in the following way:

$$\frac{\epsilon_{\text{X-CH}_3}}{\epsilon_{\text{X-CH}_2}} = \left(\frac{\epsilon_{\text{CH}_3\text{-CH}_3}}{\epsilon_{\text{CH}_2\text{-CH}_2}} \right)^{1/2} \quad (3)$$

The above formula is equivalent to the assumption that the parameter accounting for the deviation from the geometrical mean is the same for both X–aliphatics interactions.

The model parameters have been determined on the basis of the minimal data set. The data used are shown in Table 2. The number of experimental data points is exactly equal to the number of parameters to be determined. Such a procedure ensures that the predictive abilities of the model are indeed being examined. The values of the parameters determined are given in Table 3. As it is not expected for the model to give a precise description of the subcritical properties, the low-temperature data for ethane have seemed to be more reasonable to determine the parameters of the methyl group. Nevertheless, it turned out that the accuracy of the overall prediction significantly increases if the data at higher temperature are taken. The values of parameters reported previously³⁸ are slightly different as they were calculated with an assumption that the interaction energies between the aliphatic a nonalkyl group (–O–) are equal to each other. New parameters give better results for the mixtures with ethers.

The experimental data of the following properties have been used to check the predictive abilities of the model:

For pure *n*-alkanes, aliphatic monoethers, and 1-chloroalkanes, there are orthobaric densities, enthalpies of vaporization, P – ρ – T

TABLE 2: Experimental Data Used to Determine Group Parameters for the CH₃–, –CH₂–, –O–, and Cl– Groups

group	property	conditions ^a	compound(s)	exptl value	ref
CH ₃ –	ρ_l	–88.72 °C	ethane	0.5466 g·cm ³	40 ^b
	p_{sat}	–88.72 °C	ethane	101.36 kPa	41
	ρ_l	–10 °C	ethane	0.4232 g·cm ³	42
	p_{sat}	–10 °C	ethane	1859 kPa	40
–CH ₂ –	ρ_l	24.72 °C	<i>n</i> -hexane	0.65496 g·cm ³	40 ^b
	p_{sat}	24.72 °C	<i>n</i> -hexane	19.918 kPa	41
	H^E	20 °C	<i>n</i> -pentane + <i>n</i> -decane	25.5 J·mol ^{–1}	43
		$x_1 = 0.5035$			
–O–	ρ_l	26.115 °C	diethyl ether	0.7064 g·cm ³	44 ^b
	p_{sat}	26.115 °C	diethyl ether	74.719 kPa	45
	H^E	25 °C	diethyl ether + <i>n</i> -heptane	361.3 J·mol ^{–1}	46
		$x_1 = 0.500$			
Cl–	ρ_l	28.8 °C	1-chlorobutane	0.8763 g·cm ³	47 ^b
	p_{sat}	28.8 °C	1-chlorobutane	16.212 kPa	48
	H^E	25 °C	1-chlorobutane + <i>n</i> -hexane	492 J·mol ^{–1}	49
		$x_1 = 0.5073$			

^a For the Smirnova–Victorov model, the data for ethane at –10 °C have been used. Key: ρ_l , liquid orthobaric density; p_{sat} , saturated vapor pressure; H^E , excess enthalpy. ^b Interpolated.

TABLE 3: New Group Parameters of the Modified Smirnova–Victorov Model^a

groups	$r_s/\text{cm}^3\cdot\text{mol}^{-1}$	$-\epsilon_{\text{st}}/\text{J}\cdot\text{mol}^{-1}$			
		CH ₃ –	–CH ₂ –	–O–	–Cl
hole	1	0	0	0	0
CH ₃ –	1.771	606.3			
–CH ₂ –	1	753.3	1036.1		
–O–	0.425	1035.7	1353.7	4611.6	
–Cl	1.485	766.7	1002.2		1711.9

$$z = 12; \omega = 15.65 \text{ cm}^3\cdot\text{mol}^{-1}$$

^a Key: r_s , number of segments; $-\epsilon_{\text{st}}$ is an interaction energy; z , coordination number; ω , segment volume.

properties (i.e. densities as a function of pressure and temperature) of liquids and gases (vapors), and saturated vapor pressures.

For binary mixtures containing an *n*-alkane and one from among the three above-mentioned compounds, i.e., *n*-alkane + *n*-alkane, aliphatic monoether + *n*-alkane, and 1-chloroalkane + *n*-alkane, we have enthalpies of mixing, volumes of mixing, infinite dilution activity coefficients, isobaric solid–liquid equilibria, and vapor–liquid equilibria (at moderate and high pressures).

TABLE 4: Characterization of Data for Pure *n*-alkanes and for Binary Mixtures (*n*-Alkane + *n*-Alkane) Used in Test of the Model

property = <i>f</i>	<i>f</i> (<i>x</i> , <i>y</i> = const)			no. of		range of		compounds ^a
	<i>f</i>	<i>x</i>	<i>y</i>	systems	points	<i>x</i>	<i>y</i>	
liquid density	ρ	<i>p</i>	<i>T</i>	159	2238	0.1–800 MPa	223–573 K	2–40
orthobaric liquid density	ρ_l	<i>T</i>		32	1020	90–658 K		2–20
orthobaric vapor density	ρ_g	<i>T</i>		11	402	88–533 K		2–7
compressibility factor	<i>Z</i>	<i>p</i>	<i>T</i>	51	783	0.7–69 MPa	273–663 K	2–8
saturated vapor pressures	p_{sat}	<i>T</i>		72	1667	94–626 K		2–28
enthalpy of vaporization	ΔH_v	<i>T</i>		18	112	260–444 K		2–19
excess enthalpy	H^E	<i>x</i> ₁	<i>T</i>	49	468	0–1	283–379 K	5–36
excess vol	V^E	<i>x</i> ₁	<i>T</i>	72	657	0–1	293–399 K	6–36
infinite dilution activity coeff	γ^∞	<i>T</i>		121	267	293–423 K		3–36
solubility temp	<i>T</i>	<i>x</i> ₁		26	425	0–1		5–36
saturated vapor pressure (low pressure)	p_{sat}	<i>x</i> ₁	<i>T</i>	13	112	0–1	128–370 K	2–16
boiling temp (low pressure)	<i>T</i> _b	<i>x</i> ₁	<i>p</i>	26	214	0–1	1.3–101 kPa	6–16
vapor phase composition (low pressure)	<i>y</i> ₁	<i>x</i> ₁		11	82	0–1		2–16
saturated vapor pressure (high pressure)	p_{sat}	<i>x</i> ₁	<i>T</i>	62	512	0–1	255–573 K	2–20
boiling temp (high pressure)	<i>T</i> _b	<i>x</i> ₁	<i>p</i>	5	43	0–1	6.9–30.6 bar	2–7
vapor phase composition (high pressure)	<i>y</i> ₁	<i>x</i> ₁		61	505	0–1		2–20

^a The range of numbers of carbon atoms in the *n*-alkane molecules.**TABLE 5: Characterization of Data for Pure *n*-monoethers and for Binary Mixtures (*n*-Monoether + *n*-Alkane) Used in a Test of the Model**

property = <i>f</i>	<i>f</i> (<i>x</i> , <i>y</i> = const)			no. of		range of		compounds ^a
	<i>f</i>	<i>x</i>	<i>y</i>	systems	points	<i>x</i>	<i>y</i>	
liquid density	ρ	<i>p</i>	<i>T</i>	44	545	0.1–1216 MPa	293–561 K	4–10
orthobaric liquid density	ρ_l	<i>T</i>		35	110	288–374 K		4–12
saturated vapor pressures	p_{sat}	<i>T</i>		17	372	195–501 K		2–11
enthalpy of vaporization	ΔH_v	<i>T</i>		22	53	248–363 K		2–12
excess enthalpy	H^E	<i>x</i> ₁	<i>T</i>	33	626	0–1	298 K	4–16; 6–16
excess vol	V^E	<i>x</i> ₁	<i>T</i>	18	317	0–1	288–308 K	5–8; 6–16
infinite dilution activity coeff (ether)	γ^∞	<i>T</i>		1	2	373, 393 K		8; 28
infinite dilution activity coeff (<i>n</i> -alkane)	γ^∞	<i>T</i>		4	13	296–323 K		16; 5–7
solubility temp	<i>T</i>	<i>x</i> ₁		12	274	0–1		4–8; 8–24
saturated vapor pressure (low pressure)	p_{sat}	<i>x</i> ₁	<i>T</i>	6	70	0–1	308–363 K	4–8; 6–9
vapor phase composition (low pressure)	<i>y</i> ₁	<i>x</i> ₁		5	61	0–1		4–8; 6–9
saturated vapor pressure (high pressure)	p_{sat}	<i>x</i> ₁	<i>T</i>	11	135	0–1	283–414 K	2; 4
vapor phase composition (high pressure)	<i>y</i> ₁	<i>x</i> ₁		11	135	0–1		2; 4

^a The range of numbers of carbon atoms in the ether molecules (first range) and in the *n*-alkane molecules (second range).**TABLE 6: Characterization of Data for Pure 1-Chloroalkanes and for Binary Mixtures (1-Chloroalkane + *n*-Alkane) Used in a Test of the Model**

property = <i>f</i>	<i>f</i> (<i>x</i> , <i>y</i> = const)			no. of		range of		compounds ^a
	<i>f</i>	<i>x</i>	<i>y</i>	systems	points	<i>x</i>	<i>y</i>	
liquid density	ρ	<i>p</i>	<i>T</i>	61	485	0.1–1216 MPa	253–423 K	1–5
orthobaric liquid density	ρ_l	<i>T</i>		30	370	173–423 K		1–16
orthobaric vapor density	ρ_g	<i>T</i>		1	22	308–413 K		1
compressibility factor	<i>Z</i>	<i>p</i>	<i>T</i>	19	508	0.1–31.4 MPa	308–498 K	1
saturated vapor pressures	p_{sat}	<i>T</i>		15	212	183–600 K		1–16
enthalpy of vaporization	ΔH_v	<i>T</i>		9	24	298–368 K		2–16
excess enthalpy	H^E	<i>x</i> ₁	<i>T</i>	29	472	0–1	298–308 K	4–16; 6–16
excess vol	V^E	<i>x</i> ₁	<i>T</i>	67	826	0–1	293–318 K	3–18; 5–16
infinite dilution activity coeff (chloroalkane)	γ^∞	<i>T</i>		30 ^b	105 ^b	293–367 K		3–7; 8–36
infinite dilution activity coeff (<i>n</i> -alkane)	γ^∞	<i>T</i>		8	28	293–343 K		4–18; 5–7
solubility temp	<i>T</i>	<i>x</i> ₁		8	252	0–1		4, 8; 18–24
saturated vapor pressure (low pressure)	p_{sat}	<i>x</i> ₁	<i>T</i>	11	167	0–1	298–353 K	4; 6, 7
boiling temp (low pressure)	<i>T</i> _b	<i>x</i> ₁	<i>p</i>	1	19	0–1	94.4 kPa	4; 6
vapor phase composition (low pressure)	<i>y</i> ₁	<i>x</i> ₁		8	136	0–1		4; 6, 7

^a The range of numbers of carbon atoms in the chloroalkane molecules (first range) and in the *n*-alkane molecules (second range). ^b Seven of the systems with 23 experimental points are for mixtures of two chloroalkanes.

A significant part of the experimental data reported in the literature has been used. Their characterization is given in Tables 4–6. The great number of the experimental data makes an accuracy of particular data sets not to be so important as it happens if only a few systems are selected to test a model.

Nevertheless, the data exhibiting an evident poor accuracy were rejected from the database. Data for the multicomponent systems are not included. There are scarce and concern mainly the vapor–liquid equilibria for alkanes. On the other hand, in the group-contribution approach, the multicomponent properties do

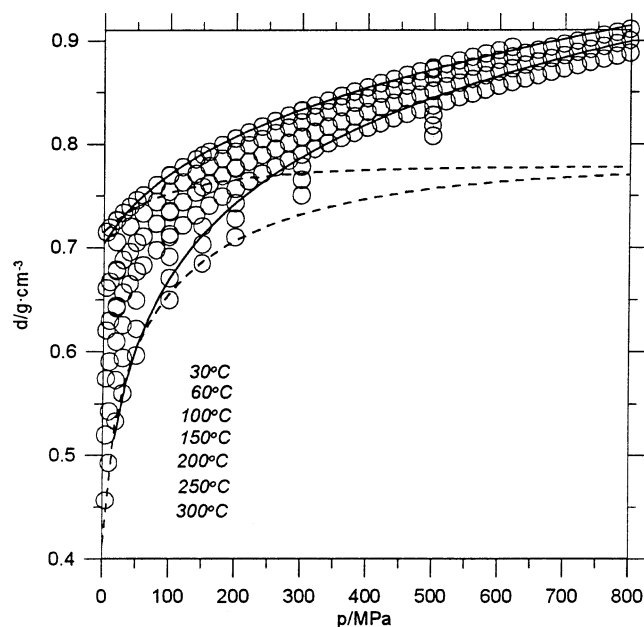


Figure 1. Prediction of density of *n*-nonane as a function of pressure at temperatures 30, 60, 100, 150, 200, 250, and 300 °C. Circles denote experimental data.^{50,51} Lines are predicted at 30 and 300 °C by the cell-hole model (solid) and the simplified Smirnova-Victorov model³⁸ (dashed).

not represent a new quality with respect to the binary ones and no additional difficulties are expected if such data are to be predicted.

The mean integral deviation between the experimental and the model dependence was used as a measure of the prediction accuracy. It is defined as follows:³⁸

$$\sigma = \left(\frac{\int_{x_{\min}}^{x_{\max}} |f(x)^{\text{calcd}} - f(x)^{\text{expt}}| dx}{x_{\max} - x_{\min}} \right) \quad (4)$$

where both the model (calcd) and the experimental (expt) functions were estimated by a polygon.

The detailed results are collected in Table 9, where the deviations for the new model are also included. Here only the main conclusions are formulated.

(i) It is clear that the Smirnova-Victorov model is able to give at least a qualitative thermodynamic description of pure normal alkanes, unbranched monoethers, 1-chloroalkanes, and their mixtures with *n*-alkanes. In light of the diversity of properties being predicted, the quality of the description is impressive.

(ii) There exist two fields in which the model fails to give the fully satisfactory results:

- At low temperatures and under high pressures it considerably underestimates liquid densities. The high-pressure limit of a model applicability varies between 100 and 500 MPa, depending on the compound and temperature (Figure 1).

- The description of the saturated vapor pressures of pure substances, although qualitatively correct, does not guarantee a sufficient accuracy of the vapor-liquid equilibria for mixtures.

4. The Model Improvement

The results of the application of the Smirnova-Victorov model for the systems formed from the basic chain molecules give a good insight into abilities and shortcomings of the

lattice-hole (gas-lattice) theories. The main conclusion is the model's inability to reproduce liquid densities under very high pressures.

In the lattice-hole models an increase of pressure leads to a decrease of a number of holes. In the limit, the system volume reaches the sum of segment volumes which are independent of pressure and temperature. This asymptotic dependence of the liquid volume with respect to pressure could agree with reality at least quantitatively, but this is not so. The segment volume determined through the fitting to the properties under normal pressures leads always to the liquid densities which are too low at high pressures (Figure 1). In a cell-hole model, increasing the pressure similarly decreases the number of holes, but additionally makes the cell volume smaller. As a result, densities at high pressures are higher and do not exhibit a strictly asymptotic behavior. This underestimation of the high-pressure liquid densities by the lattice-hole models, results directly from the fixed cell volume which is equivalent to the constant distances between molecules. By no means it is an oversimplification which may lead to serious errors under extreme conditions. This assumption cannot be removed in the framework of the lattice-hole theory as the constancy of the cell volume is an inherent feature of any model of this kind.

In the cell-hole model, in which the cell volume is not fixed, it should be determined through maximization of the partition function which is given by eq 1.¹⁸ This leads to the following equation:⁵²

$$\omega \left(\frac{\partial \ln Q}{\partial \omega} \right)_{N,V,T} = -Z + \omega \left(\frac{\partial \ln Q_{FV}}{\partial \omega} \right)_{N,V,T} + \omega \left(\frac{\partial \ln Q_E}{\partial \omega} \right)_{N,V,T} = 0 \quad (5)$$

where Z is a compressibility factor ($=pV/\Sigma N_i kT$), Q_{FV} and Q_E stand for the free volume and the lattice energy contributions to the configurational partition function, respectively. The ideal gas limit requires the free volume contribution to satisfy the following condition:

$$\lim_{V \rightarrow \infty} \omega \left(\frac{\partial \ln Q_{FV}}{\partial \omega} \right)_{N,V,T} = \sum_i N_i \quad (6)$$

Note that the proper limit cannot be reached if the free volume term vanishes, which is what happens for the lattice-hole theories.

Up to now only a few cell-hole models with the variable cell volume for the systems formed with chain molecules have been published in the literature. These are: the model of Simha and Somcynsky,²⁶ Nies and Stroeks,²⁸ and Zhong et al.,⁹ including successive modifications and improvements. For the first two models, important differences between the free volume contributions are noted. In the model of Nies and collaborators,²⁹ the free volume term is defined as

$$Q_{FV} = \prod_{i(\text{groups})} l_i^{3c_i r_i \bar{N}_i} \quad (7)$$

while in that of Simha and Somcynsky²⁶ it is given by

$$Q_{FV} = \prod_{j(\text{molecules})} v_{f_j}^{N_j} \quad (8)$$

where l_i is a segmental free length of the i th group, which possesses r_i segments and $3c_i$ external degrees of freedom; the total number of the i th groups in the system is equal to \bar{N}_i ; v_{f_j}

is a molecular free volume and the number of external degrees of freedom (c_j) in the second equation corresponds to a whole molecule; the number of molecules is equal to N_j . At the ideal gas limit these expressions lead to

$$\lim_{V \rightarrow \infty} \omega \left(\frac{\partial \ln Q_{\text{FV}}}{\partial \omega} \right)_{N,V,T} = \sum_{i(\text{groups})} c_i r_i \bar{N}_i \text{ or } \sum_{j(\text{molecules})} c_j N_j \quad (9)$$

which do not satisfy the proper condition given by eq 6. Note that the two assumptions used to formulate the free volume contribution are independently responsible for this disagreement. Indeed, to obtain a proper limit it is simultaneously necessary to put $c_i = 1$ and also to identify $r_i \bar{N}_i$ with N_i , that is to assume a molecule to be built from one segment only, or to locate the whole molecule in one cell.

Equation 7 expresses the assumption that separate segments are located within their own cells, and their movement does not depend on a similar movement of the neighboring segments. For the chain molecules in which segments or groups are connected via chemical bonds, it is a highly unrealistic picture. To improve this assumption, an additional parameter called "the number of external degrees of freedom" was introduced to account for the restriction of movement, although its original interpretation was quite different.⁵³ An idea standing behind eq 7 originates from Flory⁵⁴ and Lee et al.⁵⁵ It is clear that a such factorization of the free volume contribution cannot be applied to the gas phase at low pressure since it leads to the groups behaving like *quasi* components.

If the external degrees of freedom are understood as the modes of orientations with respect to the environment, what agrees with an explanation given by Prigogine and co-workers,⁵³ they should disappear for density approaching zero. Therefore, it may be concluded, that also this approach of the external degrees of freedom has a sense only if applied to the condensed phase.

Hence it is clear that the usual formulations of the free volume contribution, given both by eqs 7 and 8, are erroneous. They may lead to the practical consequences which are difficult to predict. Note that for the cell-hole models, an equation-of-state, apart from the usual expression:

$$p = kT \left(\frac{\partial (\ln Q)}{\partial V} \right)_{N,T,\omega} \quad (10)$$

requires also eq 5 to be simultaneously fulfilled. At the low pressure, for the fixed cell volume ω , eq 10 approaches a proper limit. But it is not true for eq 5. As a result, an equation of state may deteriorate at low densities. And this is indeed what has been observed. An isotherm generated by a cell-hole model based on the traditional free volume is not realistic on the vapor side. Depending on a particular form of this contribution, compounds and values of the model parameters, the system of eqs 5 and 10 may be not soluble at all or leads to an absurd behavior like a region where the stability conditions are violated. Although the model fails only if applied at low pressures while formally giving a good description anywhere else, it can hardly be recognized as a correct, since an erroneous form of the free volume contribution affects all the properties.

The simplest free volume term of a multisegmental molecule is for the molecule with rigid bonds that is fully attached by the holes. For this case, it is equivalent to the spatial one. The volume of a cell for a molecule containing r_i segments is equal to $r_i \omega$. For a one-segmental, symmetric molecule, the available volume is a volume of the cell itself, i.e., ω . For a multiseg-

mental one which is bonded with fixed bonds or even for an unsymmetric molecule, the extent of available space will be again equal to that of a unitary cell. It occurs like that since the movement of all segments is strictly correlated.

Up to now the segments do not have to be identified with the molecular groups. Any nonspherical molecule can wander in an allowable space which is limited to the largest symmetric structural unit which, together with its replications, can build the whole molecule. Since, as usual, the application of Ockham's Razor is recommended, it is convenient to regard these units as the molecular groups.

For the second extreme, i.e. molecules fully attached by the occupied cells, a rigorous analytical expression for the free volume cannot be derived. Usually an approximation based on the square-well potential is used what leads to the free volume equal to a residual between the cell volume and the hard core volume of a molecule.

For a multigroup molecule, the allowable space is greater as additionally chain flexibility should be taken into account. It seems that inclusion of this factor cannot be done in a rigorous way. Nevertheless it is better to assume first a rodlike rigid molecule and then to look for some corrections, than to start with the full flexibility and a totally independent movement of groups as has been done usually.

5. New Model: Definition

Finally the new cell-hole (CH) model can be introduced and strictly defined. It should be underlined that it is the first time the cell-hole model applicable both for liquids and gases has been developed.

The cell-hole group-contribution model is a cell-hole model based on the following detailed assumptions.

(i) The combinatorial term is given by the Staverman-Guggenheim expression for the athermal contribution^{15,17} and the Guggenheim expression for the nonrandom mixing contribution.¹⁶ The number of segments per optional group is given as a ratio of its hard core volume to that of the methylene group, i.e.

$$r_X = \frac{v_X^*}{v_{\text{CH}_2}^*} \quad (11)$$

although for the ether group an arbitrary higher value is proposed. The coordination number z is equal to 12, and the hole is assumed to be built from one segment. The number of external contacts per group is given by the usual formula:

$$q_X = r_X(z - 2) + 2 \quad (12)$$

(ii) The molecular free volume is given by

$$\ln v_i = (1 - \bar{y}_{i0}) \ln[\omega(1 + n_i c) - \bar{v}_i^*] + \bar{y}_{i0} \ln[\omega(1 + n_i c)] \quad (13)$$

where \bar{y}_{i0} is an average fraction of holes around the i molecule, ω is a cell volume, n_i is the number of bonds in a molecule, and c stands for an empirical parameter, called as the chain flexibility factor, which is to account for the chain flexibility.

Equation 13 expresses an average between two states of a molecule — being attached by the occupied cells ("solidlike") or by holes only ("gaslike").²⁰ The above formula is strictly empirical, and the c parameter must be adjusted to the experimental data.

The average fraction of holes is calculated as follows:

$$\bar{y}_{i0} = \sum_{k=1} \alpha_{ki} y_{k0} \quad (14)$$

α_{ki} is a segment fraction of k groups in the i molecule and y_{k0} stands for a fraction of the (k group, hole) contact pairs in the system. The average segmental hard core volume \bar{v}_i^* is given as a ratio of a molecular hard core volume to the number of segments, i.e., $\bar{v}_i^* = v_i^*/r_i$. The following equation

$$Q_{FV} = \prod_{j(\text{molecules})} v_{f_j}^{N_j} \quad (15)$$

together with eq 13, defines the total free volume contribution which ensures the proper low-density limit given by eq 6.

(iii) The contribution to the partition function due to the lattice energy has the usual form

$$\ln Q_E = - \sum_{i \geq j} N_{ij} \phi_{ij} / kT \quad (16)$$

where summation involves all possible numbers of contacts N_{ij} . Each contact pair has assigned a potential of interaction ϕ_{ij} , which is of the Lennard-Jones form

$$\phi_{ij} = 4\epsilon_{ij}[(v_{ij}^*/\omega)^4 - (v_{ij}^*/\omega)^2] \quad (17)$$

where the hard core volumes between unlike segments (v_{ij}^*) are interrelated to those pertaining to the like contacts, by means of the following mixing rule:

$$v_{ij}^{*1/3} = \frac{1}{2}(\bar{v}_i^{*1/3} + \bar{v}_j^{*1/3}) \quad (18)$$

(iv) The most probable configuration which is defined through the numbers of unlike contact pairs N_{ij} and the value of the cell volume ω , is determined through the maximization of the partition function with respect to the above-mentioned parameters. The final equations built the system of the generalized quasichemical equations (eq 19), supplemented by eq 5.

$$X_s \sum_{t=0} \alpha_t X_t \eta_{st} \beta_{st} = 1 \quad \text{for } s = 0, 1, \dots, m \text{ (for all groups)} \quad (19)$$

where α_t is a fraction of contacts involving groups of the t type among all the zN_q contacts in the system and the β_{st} parameter is defined by

$$\beta_{ij} = \exp\left(\frac{\partial \ln Q_{FV}}{\partial N_{ij}}\right)_{N,V,T} \quad (20)$$

The parameter η_{ij} expressed by

$$\eta_{ij} = \exp(-\Delta\epsilon_{ij}/kT) \quad (21)$$

is directly related to the interchange energy $\Delta\epsilon_{ij} = \phi_{ij} - 1/2(\phi_{ii} + \phi_{jj})$, and ϕ_{ij} is the potential of interaction between the i - j contact pair (eq 17).

The numbers of contacts N_{ij} result from the vector of auxiliary variables X which is a solution of the system of eqs 19:

$$N_{ss} = 1/2 z N_q \alpha_s^2 X_s^2 \quad (22a)$$

$$N_{st} = z N_q \alpha_s \alpha_t X_s X_t \eta_{st} \beta_{st} \quad (22b)$$

The particular properties can be derived through a proper differentiation of the partition function. The equation of state

has formally the same form as given by eq 2. The main difference concerns the cell volume (ω). This parameter is fixed for the Smirnova–Victorov model while it results from the most probable configurations for the cell–hole model. Among other parameters, the chemical potential (μ_k) and the configurational energy (U) are of special interest. They are shown below:

$$\begin{aligned} \mu_k/kT = & -\ln \xi_k + \ln \frac{\varphi_k}{\bar{V}r_k} - r_k \ln \left(1 - \frac{1}{\bar{V}}\right) + \\ & \frac{z}{2}(r_k - q_k) \ln \left[1 - \frac{1}{\bar{V}} \left(\frac{q_m}{r_m} - 1\right)\right] - z r_k \ln X_0 + \\ & \frac{z}{2} \sum_{i=1}^{groups} q_i v_{ik} (2 \ln X_i - \phi_{ii}/kT) - \left(\frac{\partial \ln Q_{FV}}{\partial N_k}\right)_{N,V,T} \end{aligned} \quad (23)$$

$$U/k = \sum_{i \geq j} N_{ij} \phi_{ij} \quad (24)$$

Here r_k and q_k are the numbers of segments and external contacts per a molecule, φ_k is a segment fraction, and ξ_k expresses the number of ways in which a successive segment of the k th molecule can be oriented with respect to the previous one, and v_{ik} gives the number the i th group in a molecule of the k th compound; the explanations of other symbols follow eq 2 and 16. The mixture properties—activity coefficients and the excess functions can be calculated as residuals between the mixture and the pure compound properties. The excess volume is related directly to the volumes which result from the equation of state—eq 2. The excess enthalpy is given by

$$H^E = U^E + pV^E \quad (25)$$

The detailed expressions for derivatives of the free volume and energetic terms with respect to the number of unlike contacts (N_{ij}), the number of molecules (N_k), and the cell volume (ω), which are included in eqs 5, 20, and 23, can be derived through the direct differentiation of eqs 13–17. Their forms are as follows

$$\omega \left(\frac{\partial \ln Q_{FV}}{\partial \omega} \right)_{N,V,T} = \sum_i N_i \left[1 + \frac{\bar{v}_i^*(1 - \bar{y}_{i0})}{\omega(1 + n_i c) - \bar{v}_i^*} \right] \quad (26)$$

$$\omega \left(\frac{\partial \ln Q}{\partial \omega} \right)_{N,V,T} = \frac{8}{kT} \sum_{i \geq j} \epsilon_{ij} N_{ij} (v_{ij}^*/\omega)^2 [2(v_{ij}^*/\omega)^2 - 1] \quad (27)$$

$$\begin{aligned} \left(\frac{\partial \ln Q_{FV}}{\partial N_{k0}} \right)_{N,V,T} = \\ \frac{1}{Q_k} \sum_i N_i \alpha_{ki} \ln \left[1 + \frac{\bar{v}_i^*}{\omega(1 + n_i c) - \bar{v}_i^*} \right] \text{ for } k \neq 0 \end{aligned} \quad (28)$$

where Q_k denotes the number of contacts involving the groups of the k -type which is equal to

$$Q_k = z q_k \sum_i v_{ki} N_i \quad (29)$$

For other contact pairs, not involving the holes, this derivative

TABLE 7: Description of the Parameters of the Cell–Hole Model

type	parameter	symbol	no. of parameters
structural	hard core vol	v_X^*	one per each group
	segments per hole	r_o	universal (=1)
	segments per $-\text{CH}_2-$ group	r_{CH_2}	universal (=1)
	coordination no.	z	universal (=12)
	chain flexibility factor	c	universal (=0.065)
energetic	energy of interaction	ϵ_{st}	per each group contact

TABLE 8: Group Parameters of the Cell–Hole Model

groups	$v^*/\text{cm}^3\cdot\text{mol}^{-1}$	$\epsilon_{\text{st}}/\text{J}\cdot\text{mol}^{-1}$			
		CH_3-	$-\text{CH}_2-$	$-\text{O}-$	$-\text{Cl}$
CH_3-	17.761	813.6			
$-\text{CH}_2-$	11.734	822.8	1004.8		
$-\text{O}-$	6.011 ^a	971.1	1079.2	3081.5	
	(5.981)	(1028.8)	(1143.3)	(3523.1)	
$-\text{Cl}$	15.100	1003.5	1115.2		2119.8

^a $r_o = 0.65$.

is equal to zero.

$$\left(\frac{\partial(\ln Q_{\text{FV}})}{\partial N_n} \right)_{N,V,T} = \ln v_{f_n} - \sum_k \frac{v_{kn} y_{k0}}{\sum_j v_{kj} N_j} \sum_i N_i \alpha_{ki} \ln \left[1 + \frac{\bar{v}_i^*}{\omega(1 + n_i c) - \bar{v}_i^*} \right] \quad (30)$$

In the above equations, the summation is performed over molecules (i,j) or groups (k).

The number and type of the parameters to be determined are displayed similarly as for the Smirnova–Victorov model. Table 7 gives a list of all the model parameters which must be determined or assumed. In comparison with the simplest version of the Smirnova–Victorov model, this model has one additional

universal adjustable parameter, the chain flexibility factor, which was determined through an approximate adjustment to an equimolar excess volume of the n -hexane + n -decane system at 25 °C.⁵⁶ The description of model parameters for alkanes (A) and an optional group attached to an aliphatic chain (X) which must be fitted to the experimental data, are given in Table 1. The parameters for the groups $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{O}-$, and $-\text{Cl}$, and those pertaining to the contact pairs between them have been determined in the same manner as described for the Smirnova–Victorov model. The validity of eq 3 has been also assumed. The properties of ethane at -88.72 °C were taken to calculate parameters of the methyl group (Table 2).

The calculated group parameters are shown in Table 8. The group parameters for the $-\text{O}-$ group, derived according to the above scheme and given in parentheses in the table, still give considerable deviations for the excess volume data for the systems containing ethers, although about 35% lower than resulted from the Smirnova–Victorov model. It seems that localization of the small ether group between two larger aliphatic ones greatly influences the volumetric properties of the ethers. It seems that a free space attached to the ether group should be relatively greater than for other groups and similarly the number of segments (r_o) should be higher than that resulting from the simple ratio of hard core volumes. New parameters, shown in Table 8 without parentheses, were calculated on the basis of an arbitrary assumption that the parameter r_o is equal to 0.65 (instead of about 0.51). As a result of this procedure, the description of the excess volumes have been improved while other properties have remained almost unaffected.

6. New Model: Application

The results are compared with those obtained by means of the Smirnova–Victorov model, including the original, multi-parameter version⁷ which, because of lack of parameters, is applicable only for alkanes. Additionally, a comparison with the commonly used methods: the modified UNIFAC¹ and the Nitta–Chao method⁵ is also presented.

TABLE 9: Prediction Accuracy (Mean Integral Deviations) of the Cell–Hole Model (CH) for Pure n -Alkanes, Ethers, and 1-Chloroalkanes and Their Mixtures with n -Alkanes^a

properties ^b	f	n -alkane; n -alkane + n -alkane					ether; ether + n -alkane				chloroalkane; chloroalkane + n -alkane				units
		CH	SV	SVor	UNI	NC	CH	SV	UNI	NC	CH	SV	UNI	NC	
1	ρ	0.015	0.033	0.032		0.007	0.013	0.091		0.015	0.020	0.157		0.054	$\text{g}\cdot\text{cm}^{-3}$
2	ρ_l	0.014	0.018	0.016			0.012 ^c	0.012 ^c		0.006 ^c	0.024	0.025			$\text{g}\cdot\text{cm}^{-3}$
3	ρ_g	3.7	6.3	7.5							25	33			$\text{g}\cdot\text{dm}^{-3}$
4	Z	0.040	0.030	0.035							0.053	0.072			
5	p_{sat}	18	36	49			28	50			37	60			kPa
6	ΔH_v	1.5 ^c	1.5 ^c	1.7 ^c			1.5 ^c	2.0 ^c		3.0 ^c	1.8 ^c	2.5 ^c		3.6 ^c	$\text{kJ}\cdot\text{mol}^{-1}$
7	H^E	15	15	19	34	16	22	25	41	47	30	29	33	18	$\text{J}\cdot\text{mol}^{-1}$
8	V^E	0.028	0.051	0.036		0.236	0.014	0.12		0.058	0.044	0.036		0.043	$\text{cm}^3\cdot\text{mol}^{-1}$
9	γ^∞	0.028 ^c	0.035 ^c	0.026 ^c	0.027 ^c	0.023 ^c	0.046 ^c	0.025 ^c	0.027 ^c	0.066 ^c	0.082 ^c	0.084 ^c	0.073 ^c	0.099 ^c	
9'	γ^∞						0.037 ^c	0.072 ^c	0.020 ^c	0.030 ^c	0.064 ^c	0.094 ^c	0.120 ^c	0.045 ^c	
10	T	0.43	0.49	0.47	0.53	0.48	0.59	0.63	0.96	1.5	0.58	0.56	0.57	0.90	K
11	p_{sat}	0.27	0.26	0.25	0.23	0.22	1.7	1.6	1.7	2.3	1.6	1.6	1.2	0.31	kPa
	T_b	1.5	1.5	1.5	1.5	1.5					0.72	0.73	1.33	0.68	K
	y_1	0.009	0.009	0.009	0.009	0.008	0.014	0.014	0.012	0.014	0.0135	0.0135	0.011	0.007	
12	p_{sat}	1.15	1.60	5.63			2.56	1.41							bar
	T_b	1.5	7.8	6.9											K
	y_1	0.023	0.018	0.019			0.037	0.044							

^a Key: f , experimental dependence in the form $f(x, y = \text{const})$, for the variables and the compounds included—see Tables 4–6; s , number of systems; pts, number of experimental points; SV, the simplified Smirnova–Victorov model;³⁸ SVor, the original Smirnova–Victorov model;⁷ UNI, the modified UNIFAC model;¹ NC, the Nitta–Chao method.⁵ ^b Description of the properties (f): (1) liquid density (P – ρ – T); (2) liquid orthobaric density; (3) vapor orthobaric density; (4) gas and vapor compressibility factor; (5) saturated vapor pressure; (6) enthalpy of vaporization; (7) excess enthalpy; (8) excess volume; (9, 9'), infinite dilution activity coefficient (9, for the first component; 9', for the second component); (10) solubility temperature of isobaric solid–liquid equilibria; (11, 12) vapor pressure of mixture (isothermal data) and boiling point temperature (isobaric data), and vapor phase composition (11, low-pressure data calculated by the γ – ϕ approach; 12, high-pressure data calculated by the equation-of-state).

^c RMSD shown, since the data sets consist mainly single experimental points.

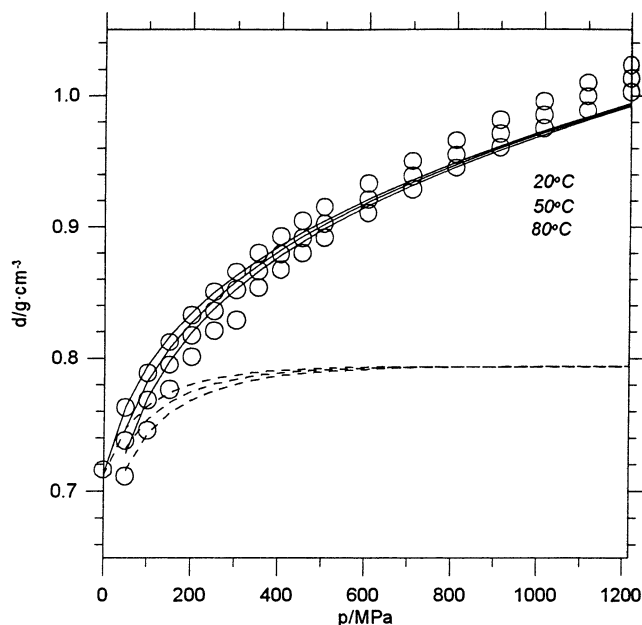


Figure 2. Prediction of density of diethyl ether at 20, 50, and 80 °C as a function of pressure. Circles denote experimental data.⁵⁷ Lines are predicted by the cell-hole model (solid) and the simplified Smirnova-Victorov model³⁸ (dashed).

Table 9 gives a summary of the overall prediction of the experimental data included in the database and described in Tables 4–6. Some characteristic groups of systems are also illustrated by figures and commented.

Liquid P – ρ – T Properties. The failure of the Smirnova-Victorov model to describe the high-pressure P – ρ – T properties for liquids was the main reason for introducing the free volume term into the model. Therefore, for these properties a considerable improvement is expected. It is believed that the remaining data will be predicted with an accuracy at least not less than that given by the Smirnova-Victorov model.

Indeed, the overall prediction accuracy of the liquid densities for the new model is about twice better for n -alkanes, and about seven (!) times better for ethers and 1-chloroalkanes (Table 9). Figure 1 shows the pressure dependence of density for n -nonane at different temperatures in the range exceeding 200 K. Densities of diethyl ether up to very high pressures (1200 MPa) at 20, 50, and 80 °C are given in Figure 2. It is encouraging that the new model gives proper densities even under extremely high pressures. It is confirmed also by the results for 1-chloroalkanes, as is shown for chloroethane, 1-chloropropane, and 1-chlorobutane at 50 °C in Figure 3. Also an increase of differences between densities for these compounds for increasing pressure is properly predicted by the model.

Gas and Vapor Compressibility Factors. The compressibility factor for n -alkanes is the only property for which prediction of the cell-hole model is significantly worse than that obtained by the Smirnova-Victorov model. As may be concluded from Figure 4, in which compressibilities of gaseous propane are shown, such worsening occurs mainly for the high-temperature data. Nevertheless, the obtained accuracy can still be considered as satisfactory.

Saturated Vapor Pressures. The cell-hole model offers a considerable improvement over the results of the Smirnova-Victorov model. For three groups of the systems, the mean deviation is about twice less than for the former method. Data and results of the prediction for n -alkanes are presented in Figure 5, for ethers in Figure 6, and for 1-chloroalkanes in Figure 7.

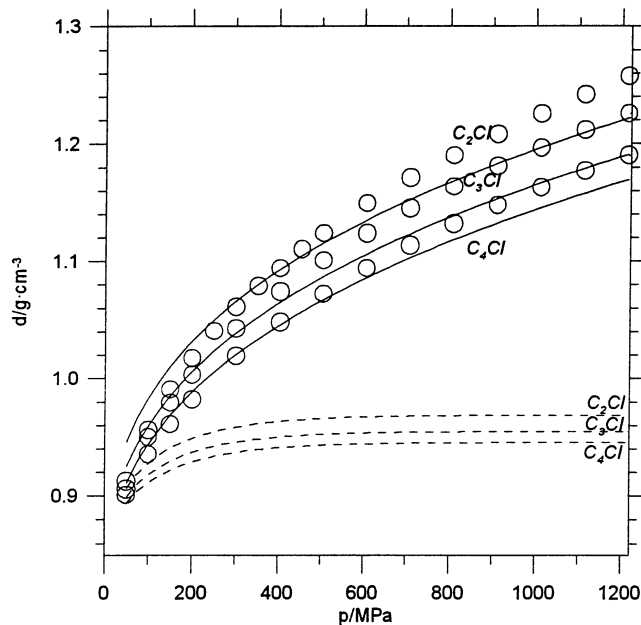


Figure 3. Prediction of density of chloroethane (C_2Cl), 1-chloropropane (C_3Cl), and 1-chlorobutane (C_4Cl) at 50 °C as a function of pressure. Circles denote experimental data.^{58,59} Lines are predicted by the cell-hole model (solid) and the simplified Smirnova-Victorov model³⁸ (dashed).

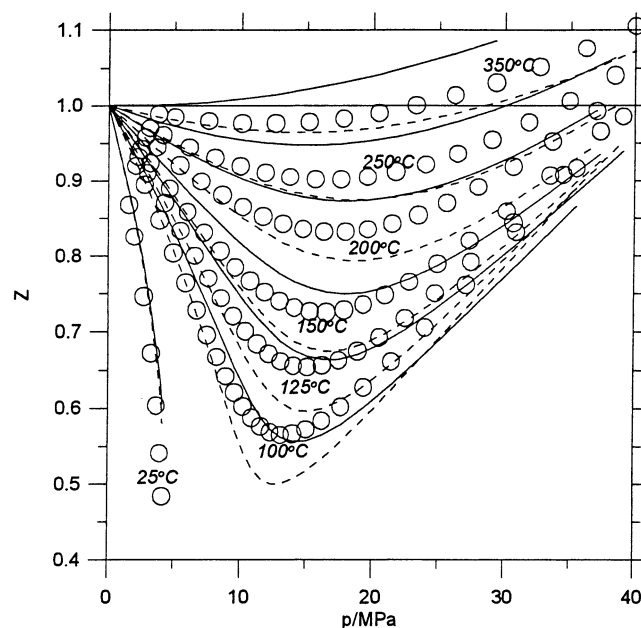


Figure 4. Prediction of the compressibility factor ($Z = pV/nRT$) of gaseous ethane at 25, 100, 125, 150, 200, 250, and 350 °C. Circles denote experimental data.⁶⁰ Lines are predicted by the cell-hole model (solid) and the simplified Smirnova-Victorov model³⁸ (dashed).

The significantly better performance of the cell-hole model also at low pressures (and low temperatures) is evident.

Good results for the saturated vapor pressures are worth emphasizing. However, further improvement would still be desired here, particularly for some long-chained compounds and for dimethyl ether as well, for which systematic deviations can be observed.

Excess Enthalpies. Mixing functions for the binary systems of two alkanes attracted a great attention in the past. Thanks to this, quite a large set of experimental data exists both for excess enthalpies and excess volumes.

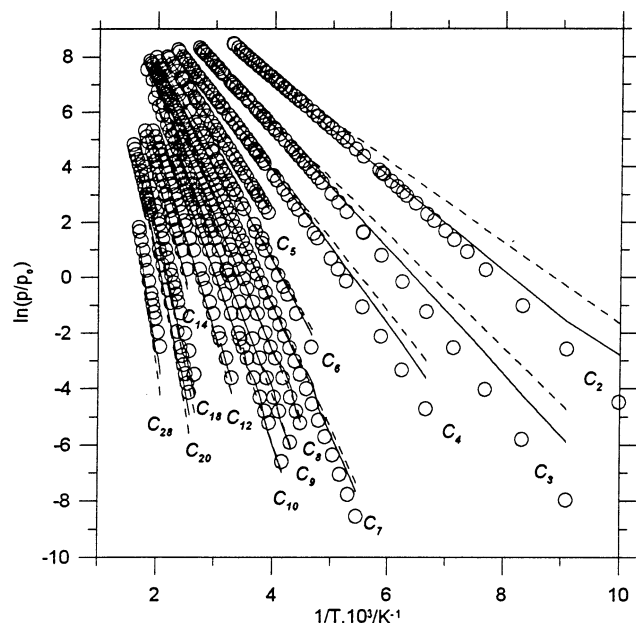


Figure 5. Prediction of saturated vapor pressures of C_2 – C_{10} , C_{12} , C_{14} , C_{18} , C_{20} , and C_{28} normal alkanes. Circles denote experimental data for: (C_2 – C_6 , C_8 – C_{10} , C_{12} , C_{14}),⁴¹ C_7 ,⁶¹ C_{18} ,⁶² C_{20} ,⁶³ C_{28} .⁶⁴ Lines are predicted by the cell–hole model (solid) and the simplified Smirnova–Victorov model³⁸ (dashed); p_0 is a reference pressure equal to 1 kPa.

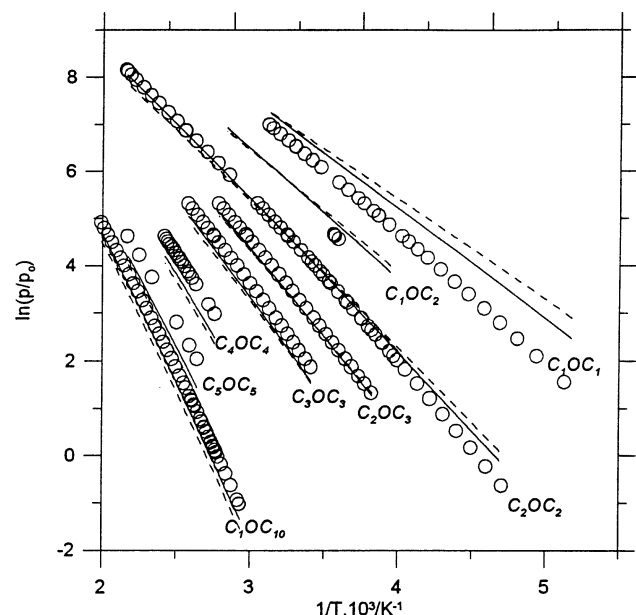


Figure 6. Prediction of saturated vapor pressures of some aliphatic ethers: dimethyl (C_1OC_1), methyl ethyl (C_1OC_2), diethyl (C_2OC_2), ethyl propyl (C_2OC_3), dipropyl (C_3OC_3), dibutyl (C_4OC_4), dipentyl (C_5OC_5), and methyl decyl ether (C_1OC_{10}). Circles denote experimental data for dimethyl ether,^{65,66} methyl ethyl ether,⁶⁷ diethyl ether,^{45,68} (ethyl propyl ether),^{69,70} dipropyl ether,⁷⁰ dipentyl ether,⁷¹ and methyl decyl ether.⁶⁹ Lines are predicted by the cell–hole model (solid) and the simplified Smirnova–Victorov model³⁸ (dashed); p_0 is a reference pressure equal to 1 kPa.

The basic system is that of n -hexane + n -hexadecane, for which excess enthalpies were measured at numerous different temperatures. Figure 8 shows properties of this system at temperatures from 20 up to 76 °C. The observed enthalpic effects are usually explained qualitatively by breaking the structure if small molecules are mixed with long-chained ones. As a result, the average distances between molecules increase, leading to an endothermic effect. It is similar to the so-called “Patterson effect”.⁸⁰

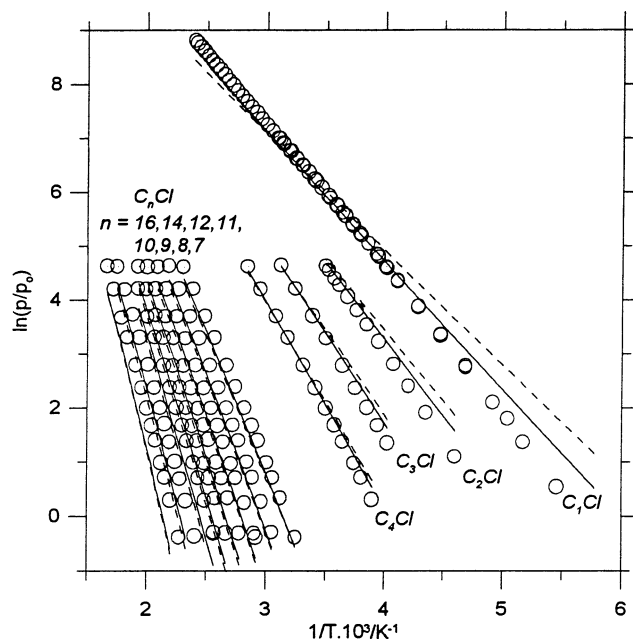


Figure 7. Prediction of saturated vapor pressures of some 1-chloroalkanes ($1-C_nH_{2n+1}Cl$, $n = 1$ –4, 8–12, 14, 16). Circles denote experimental data for: chloromethane^{72–75} and chloroethane;⁷⁶ data for all remaining 1-chloroalkanes are from Kemme and Krepes.⁴⁸ Lines are predicted by the cell–hole model (solid) and the simplified Smirnova–Victorov model³⁸ (dashed); p_0 is a reference pressure equal to 1 kPa.

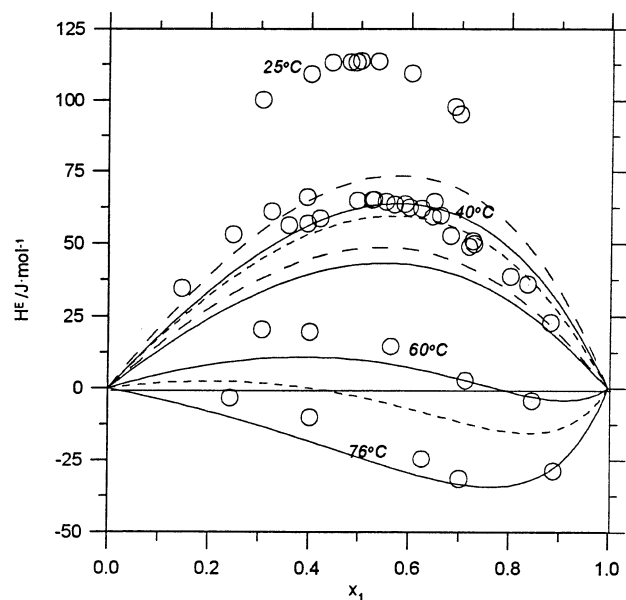


Figure 8. Prediction of excess enthalpies of the n -hexane + n -hexadecane system at 25, 40, 60, and 76 °C with respect to a mole fraction of the first component (x_1). Circles denote experimental data (°C): 25,⁷⁷ 40,^{78,79} 60,⁷⁹ 76.⁷⁹ Lines are predicted by the cell–hole model (solid), the simplified Smirnova–Victorov model³⁸ (dashed), and the Nitta–Chao model⁵ (long dash). For the last two models only limiting curves at 25 and 76 °C are shown.

In light of the complicated background of this property, the results of the cell–hole model prediction can be recognized as quite good. The model is able, at least qualitatively, to account for a complicated temperature dependence, significantly better than the Smirnova–Victorov model does. Nevertheless, excess enthalpies at lower temperatures are underestimated. It seems that the Patterson-like effect, as directly connected with the chain structure, cannot be precisely described by the solution-of-groups concept. It is interesting to notice that the Nitta–Chao method

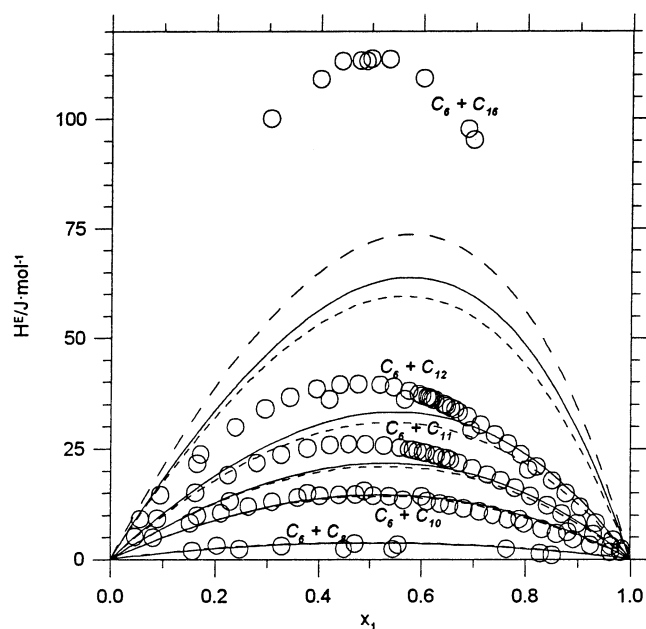


Figure 9. Prediction of excess enthalpies of the *n*-hexane + (*n*-octane, *n*-decane, *n*-undecane, *n*-dodecane, or *n*-hexadecane) systems at 25 °C with respect to a mole fraction of the first component (x_1). Circles denote experimental data of (C₆+): C₈,^{81,82} C₁₀,^{56,81} C₁₁,⁸³ C₁₂,^{84,85} C₁₆.⁷⁷ Lines are predicted by the cell-hole model (solid), the simplified Smirnova-Victorov model³⁸ (dashed), and the Nitta-Chao model⁵ (long dash, for the *n*-hexane + *n*-hexadecane only).

gives totally unacceptable results, although decreasing the excess enthalpies with increasing of temperature is properly predicted. Underestimation of the temperature dependence of the excess enthalpy if two alkanes differing greatly as to the chain length are mixed, leads to even greater underestimation of the excess heat capacity for the same systems.

Figure 9 shows excess enthalpies for mixtures containing *n*-hexane at 25 °C. For a relatively short second component, the prediction is good for all the models. The *n*-hexane + *n*-hexadecane system escapes from the smooth tendency because of an effect similar to that of Patterson.

An example of a few excess enthalpy data sets at different pressures are illustrated in Figure 10 for the *n*-hexane + *n*-decane system at 25 °C. Prediction of the cell-hole model is very good, slightly better than given by the Smirnova-Victorov model and significantly better than generated by the Nitta-Chao one.

The systems containing one polar component are relatively easier to describe. The overall prediction accuracies for the hole models are here similar, slightly better for the cell-hole model if the systems with ethers are concerned. Figure 11 shows excess enthalpies of mixtures of diethyl ether with different *n*-alkanes at 25 °C. The excellent results of the cell-hole and the Smirnova-Victorov models are particularly visible if failure of the UNIFAC model is recalled.

All three models give similar results for the 1-chloroalkane + *n*-alkane systems. The observed deviations are higher than for other groups of systems, which can be partly explained by higher absolute values of the excess enthalpies observed (Figure 12).

Generally, excess enthalpies are predicted by the cell-hole model with sufficient accuracy, except mixtures of two *n*-alkanes differing greatly as to the size and at lower temperatures. To remove this deficiency, far-reaching changes in the model assumptions would be necessary.

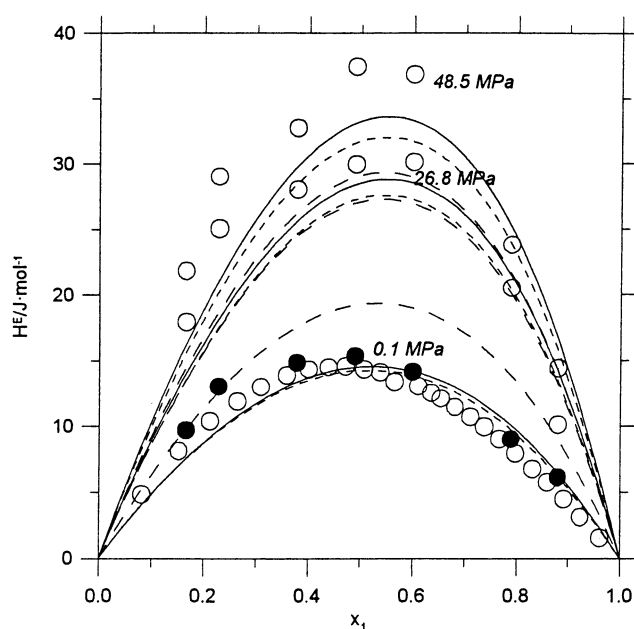


Figure 10. Prediction of excess enthalpies of the *n*-hexane + *n*-decane system at 25 °C under different pressures with respect to a mole fraction of the first component (x_1). Circles denote experimental data: (hollow),⁸¹ and (filled).⁵⁶ Lines are predicted by the cell-hole model (solid), the simplified Smirnova-Victorov model³⁸ (dashed), and the Nitta-Chao model⁵ (long dash).

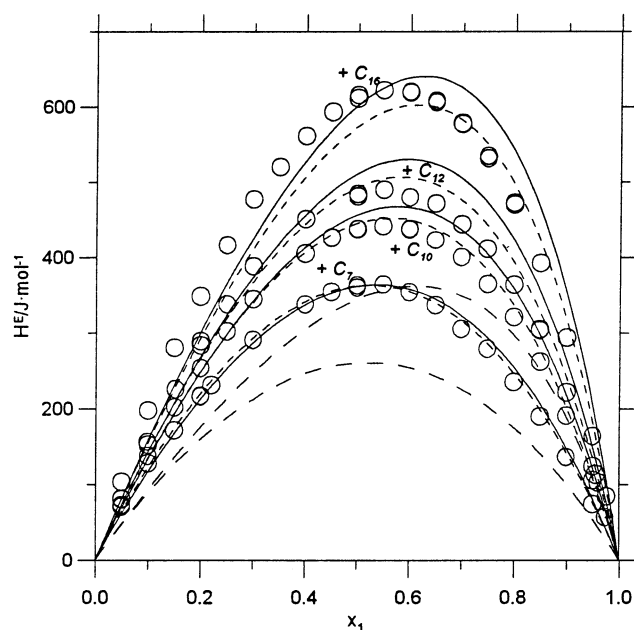


Figure 11. Prediction of excess enthalpies of the diethyl ether + (*n*-heptane, *n*-decane, *n*-dodecane, or *n*-hexadecane) systems at 25 °C with respect to a mole fraction of the first component (x_1). Circles denote experimental data.⁴⁶ Lines are predicted by the cell-hole model (solid), the simplified Smirnova-Victorov model³⁸ (dashed), and the modified UNIFAC model¹ (long dash, for the first and last systems only).

Excess Volumes. Excess volumes for binary mixtures of alkanes were studied extensively in the past. Also for other systems a considerable amount of the experimental data exist. Unfortunately, for the last groups of systems, the data at temperatures other than 25 °C are lacking. Contrary to the excess enthalpies, excess volumes for the *n*-alkane + *n*-alkane systems reveal relatively simple dependencies. The values of excess volumes are negative, decreasing if differences between two components or temperature increase.

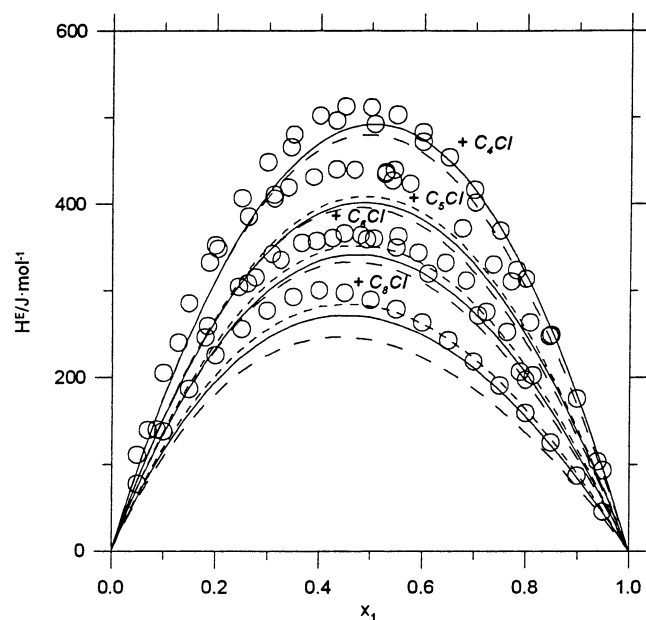


Figure 12. Prediction of excess enthalpies of the (1-chlorobutane, 1-chloropentane, 1-chlorohexane, and 1-chlorooctane) + *n*-hexane systems at 25 °C with respect to a mole fraction of the first component (x_1). Circles denote experimental data: for 1-chlorobutane +;^{49,86} 1-chloropentane +;⁸⁷ 1-chlorohexane +;^{88,89} 1-chlorooctane +.⁸⁶ Lines are predicted by the cell-hole model (solid), the simplified Smirnova-Victorov model³⁸ (dashed), and the modified UNIFAC model¹ (long dash).

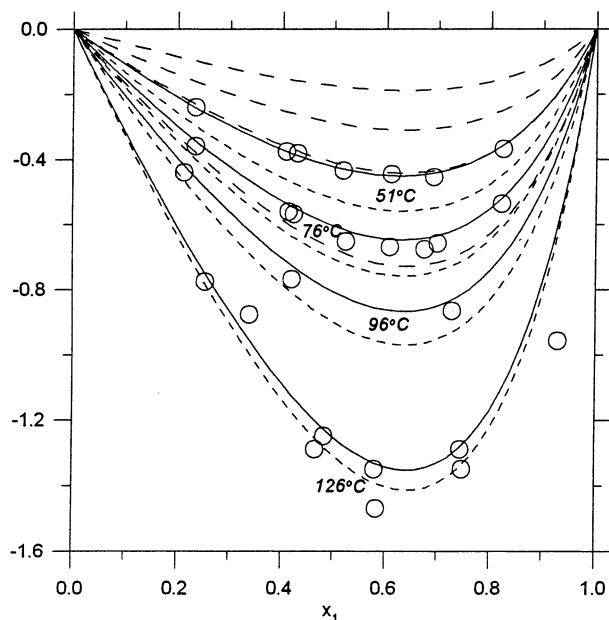


Figure 13. Prediction of excess volumes of the *n*-nonane + *n*-tetracosane (C_{24}) systems at 51, 76, 96, and 126 °C with respect to a mole fraction of the first component (x_1). Circles denote experimental data of Holleman.⁹⁰ Lines are predicted by the cell-hole model (solid), the simplified Smirnova-Victorov model³⁸ (dashed), and the Nitta-Chao model⁵ (long dash).

The cell-hole model gives excess volumes for the *n*-alkane + *n*-alkane systems which are almost twice as accurate than those of the Smirnova-Victorov model. The results of the Nitta-Chao method are rather unacceptable. Excess volumes for the *n*-nonane + *n*-tetracosane system as a function of composition are shown in Figure 13. Both the hole models provide a very good prediction.

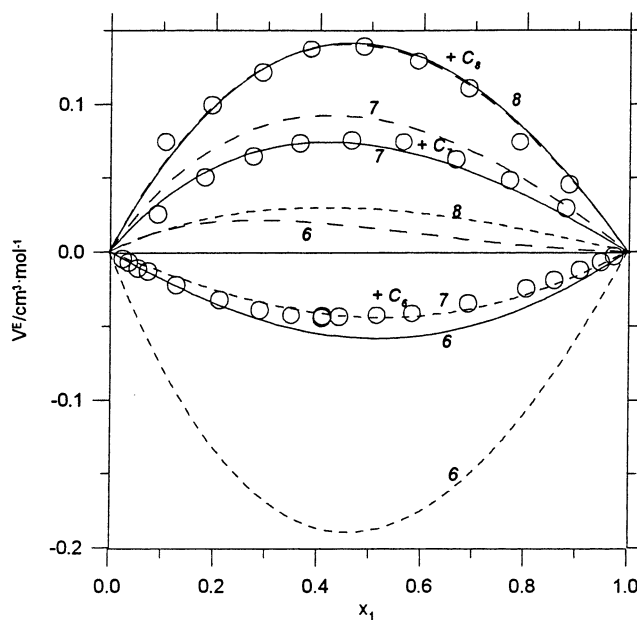


Figure 14. Prediction of excess volumes of the dibutyl ether + (C_6 , C_7 , or C_8 normal alkane) systems at 25 °C with respect to a mole fraction of the first component (x_1). Circles denote experimental data: + *n*-hexane;⁹¹ + *n*-heptane;⁹² + *n*-octane.⁹³ Lines are predicted by the cell-hole model (solid), the simplified Smirnova-Victorov model³⁸ (dashed), and the Nitta-Chao model⁵ (long dash). The curves are labeled by a number equal to the number of carbon atoms in an alkane molecule.

The typical shapes of the excess volume curves for the systems with one component exhibiting stronger interactions and mixed with an *n*-alkane, are more complicated. First the excess volumes increase while the length of an alkane is increased. It happens until a maximum is reached. Next a steady decreasing is observed. This second effect leads to negative values if both components differ significantly as to the length of their molecules. In Figure 14, the excess volumes of the dibutyl ether with *n*-hexane, *n*-heptane, and *n*-octane at 25 °C are presented. Here all systems are localized on the increasing part of the alkane chain length dependence. The cell-hole model gives an excellent prediction for the ether + *n*-alkane systems, although a special modification was imposed to reach this effect while results for other models are considerably worse if not entirely unacceptable.

Figure 15 shows the excess volumes of numerous systems composed with 1-chlorobutane and an alkane. The Nitta-Chao method is more accurate than for the ether + *n*-alkane systems, but is significantly worse than two other models.

Vapor-Liquid Equilibria. The vapor-liquid equilibrium data are divided into two groups—the low-pressure data, for which the “ γ - ϕ ” approach can be applied, and the high-pressure data, for which a consequent application of an equation of state is necessary.

For the low-pressure data, the task of a model is restricted to the prediction of the activity coefficients only. Both the cell-hole and the Smirnova-Victorov models give almost identical overall deviations. Results for alkanes and ethers are similar to those given by the UNIFAC methods. Situation for the 1-chloroalkanes + *n*-alkanes mixtures is more complicated, but differences with respect to the UNIFAC are rather meaningless.

The description of the high-pressure properties is among the most important challenges which the equation of state models face. Frequently, the models are specially designed to deal solely or mainly with these properties. Figure 16 shows the high-

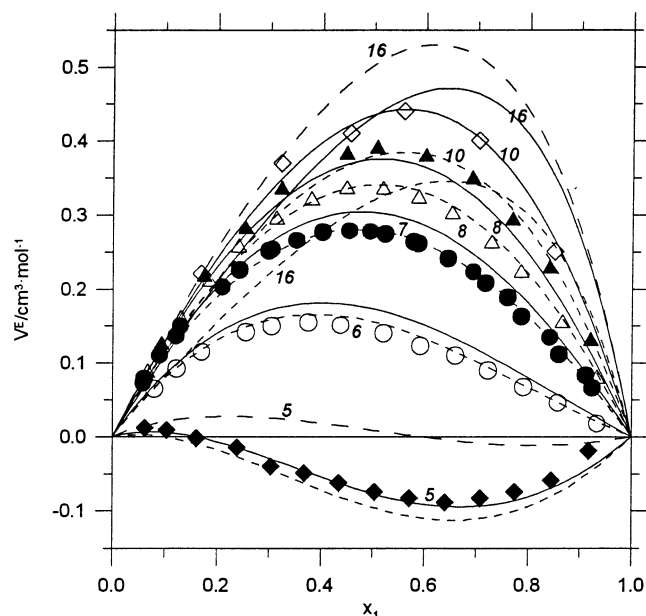


Figure 15. Prediction of excess volumes of the 1-chlorobutane + (C₅, C₆, C₇, C₈, C₁₀, C₁₂, C₁₄, or C₁₆ normal alkanes) systems at 25 °C with respect to a mole fraction of the first component (x_1). Symbols denote experimental data of 1-chlorobutane +: (◆) *n*-pentane;⁹⁴ (○) *n*-hexane;⁹⁴ (●) *n*-heptane;^{94,95} (△) *n*-octane;⁹⁴ (▲) *n*-decane;⁹⁵ (◇) *n*-hexadecane.⁹⁶ Lines are predicted by the cell-hole model (solid), the simplified Smirnova-Victorov model³⁸ (dashed), and the Nitta-Chao model⁵ (long dash). The curves are labeled by a number equal to the number of carbon atoms in an alkane molecule.

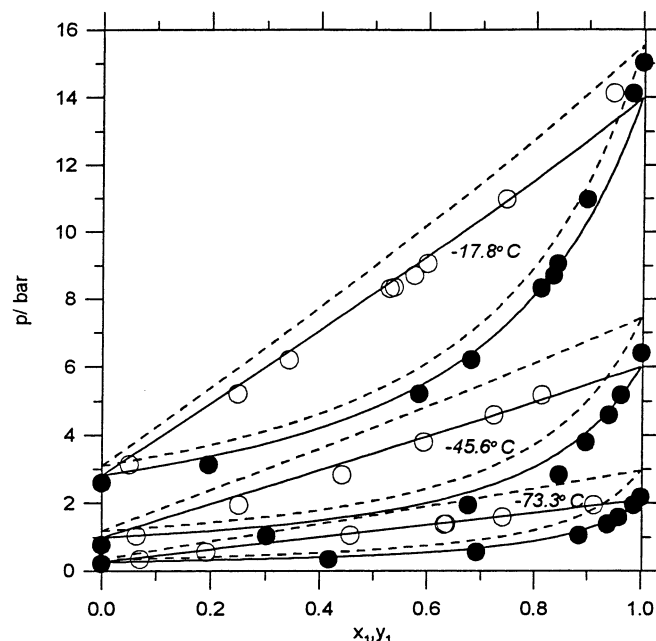


Figure 16. Prediction of vapor-liquid equilibria for the ethane + propane systems at -73.3, -45.6, and -17.8 °C with respect to a mole fraction of the first component in both phases (x_1, y_1). Circles denote experimental data.⁹⁷ Lines are predicted by the cell-hole model (solid) and the simplified Smirnova-Victorov model³⁸ (dashed).

pressure isotherms for the ethane + propane systems at lower temperatures. For all cases, the accuracy achieved by the cell-hole model is significantly better. A few isotherms for the propane + *n*-pentane systems are given in Figure 17. For the highest temperature (121.1 °C) a binary critical point appears. It is predicted by the cell-hole model, although for pressures higher than where is actually located. Figure 18 illustrates two

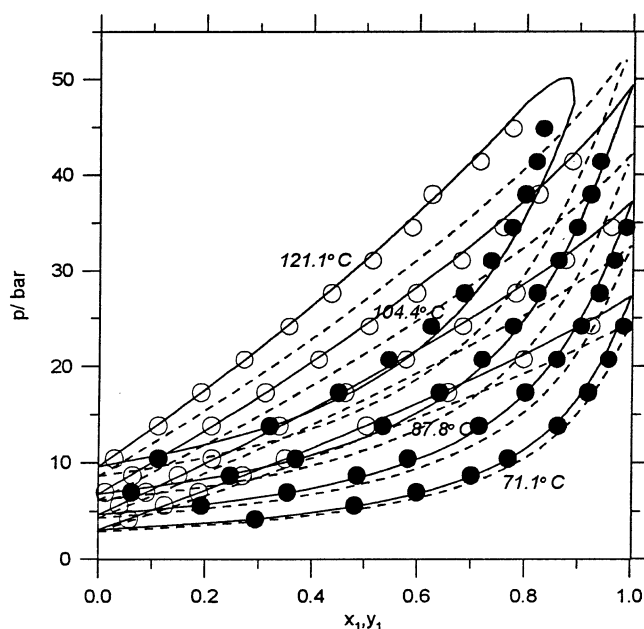


Figure 17. Prediction of vapor-liquid equilibria for the propane + *n*-pentane systems at 71.1, 87.8, 104.4, and 121.1 °C with respect to a mole fraction of the first component in both phases (x_1, y_1). Circles denote experimental data.⁹⁸ Lines are predicted by the cell-hole model (solid) and the simplified Smirnova-Victorov model³⁸ (dashed).

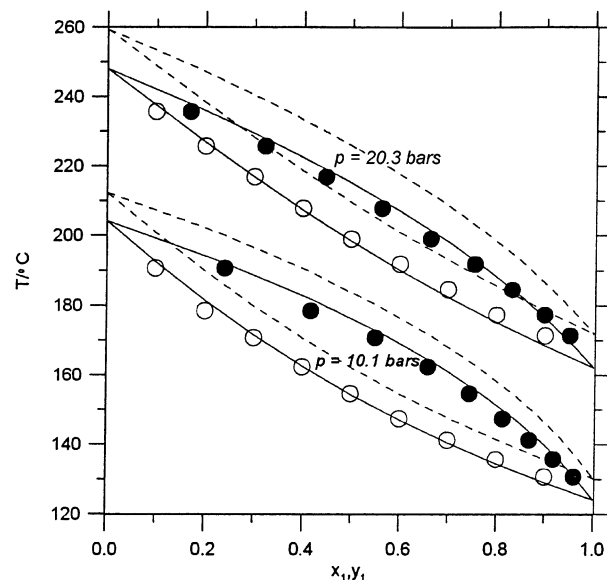


Figure 18. Prediction of vapor-liquid equilibria for the *n*-pentane + *n*-heptane systems under 10.1 and 20.3 bar with respect to a mole fraction of the first component in both phases (x_1, y_1). Circles denote experimental data.⁹⁹ Lines are predicted by the cell-hole model (solid) and the simplified Smirnova-Victorov model³⁸ (dashed).

isobars for the *n*-pentane + *n*-heptane systems under high pressures (10.1 and 20.3 bar). It is worth mentioning that the original form of the Smirnova-Victorov model with its numerous parameters, gives results even considerably worse than its simplified form.

An opposite situation occurs for the dimethyl ether + *n*-butane system for which the Smirnova-Victorov model is better. This is a consequence of the relatively high deviations of the saturated vapor pressures of dimethyl ether predicted by the cell-hole model. This compound, however, cannot be recognized as a representative for the ethers.

7. Conclusions

The free volume term, incorporated into a hole model, in the form deprived of its previous inconsistencies, has led to the group-contribution cell-hole model which is based on only a few parameters with their values determined from a few separate experimental points. This model removed the main shortcoming of any lattice-hole (gas-lattice) model, namely its inability to describe high-pressure liquid densities, and simultaneously significantly improved the prediction of some other properties of *n*-alkanes, aliphatic ethers, 1-chloroalkanes and their mixtures with *n*-alkanes. Among them the saturated vapor pressures and the high-pressure vapor-liquid equilibria are worth emphasizing.

The proposed method gives a full thermodynamic description of all configurational properties and possesses a fully predictive character. By no means is it perfect, and some disadvantages have been pointed out too. However, it still has a potential to evolve. And at least in one aspect it favorably compares with the recommended SAFT model^{9,10}—in a natural way it can be expressed in a group-contribution version.

The model gives not worse and sometimes significantly better accuracies of prediction if compared to the frequently used methods—the modified UNIFAC¹ and the Nitta-Chao⁵ models. However, it is more universal than the above-mentioned models which applicability is restricted to few properties and limited ranges of parameters only.

The systems studied in this paper are composed of relatively simple molecules. The problems and limitations which faces any application of the group-contribution approach for more complex compounds are widely recognized. They include an ambiguity of the group definition, proximity effect, strong orientational interactions, the description of branched and cyclic structures. The proposed method does not offer a solution of these problems which for some compounds are very serious. Hence, it may happen that the observed improvement may be meaningless for some properties if this model is applied to predict properties of more complicated systems. This doubt does not concern liquid densities under high pressures, which cannot be described properly by the previously reported hole-lattice models.

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Nomenclature

E_0 = lattice potential energy
 g = degeneracy factor
 H^E = excess enthalpy
 k = Boltzmann constant
 l_{fi} = segmental free length of the *i*th group
 n_i = the number of bonds in a molecule
 N_i = the number of molecules of the *i*th component
 \bar{N}_i = the total number of the *i*th groups in the system
 N_q = the product zN_q gives the total number of external contacts in the system
 N_{ij} = the number of the *i*–*j* contact pairs
 p = pressure
 p_{sat} = saturated vapor pressure
 q_i = the number of external contacts of the *i*th group (molecule)
 q_m = molar number of external contacts
 Q = configurational partition function
 Q_E = energy contribution to the partition function
 Q_{FV} = free volume contribution to the partition function

Q_k = the number of contacts involving the groups of the *k*-type
 r_i = the number of segments of the *i*th group (molecule)
 r_m = molar number of segments
 T = absolute temperature
 T_b = boiling temperature
 U = configurational internal energy
 U^E = excess internal energy
 v_{fi} = free volume of the *i*th molecule
 v_i^*, v_{ij}^* = hard core volume (segmental volume corresponding to zero of potential energy)
 \bar{v}_i^* = average molecular segmental hard core volume
 V = system volume
 \bar{V} = reduced volume (i.e. divided by the hard core volume)
 V^E = excess volume
 x_1 = mole fraction
 X_i = auxiliary variables defined by eq 19
 y_1 = mole fraction in the vapor phase
 y_{i0} = fraction of holes (empty cells) adjacent to the *i*th cell
 \bar{y}_{i0} = average fraction of holes around the *i* molecule
 z = coordination number
 Z = compressibility factor

Greek Letters

α_i = fraction of contacts involving the *i* groups in the whole system
 α_{ki} = segment fraction of *k* groups in the *i* molecule
 β_{ij} = parameter defined by eq 20
 γ^∞ = infinite dilution activity coefficient
 ΔH_v = enthalpy of vaporization
 $\Delta \epsilon_{st}$ = interchange energy between *s*–*t* groups
 ϵ_{ij} = maximum attraction energy for the Lennard-Jones potential; attraction energy of interaction for the Smirnova-Victorov model;
 ξ_i = the number of ways in which a successive segment of the *i*th molecule can be oriented with respect to the previous one
 η_{ij} = parameter defined by eq 21
 μ_i = chemical potential
 ν_{ij} = the number of *i*th groups in a molecule of the *j*th compound
 ρ = density
 ρ_g = orthobaric vapor density
 ρ_l = orthobaric liquid density
 σ = mean integral deviation
 φ_i = segment fraction
 ϕ_{ij} = potential of interaction between *i*–*j* molecules (segments, groups)
 ω = cell volume

Note Added after ASAP Posting. This article was published ASAP on 1/22/2004 with misprinted curves in Figure 18. The correct version was posted on 1/27/2004.

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