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An Analytical Method of Predicting Lee–Kesler–Plöcker Equation-of-State Binary Interaction Coefficients

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An analytical method is proposed for finding numerical values of binary interaction coefficients for the Lee–Kesler–Plöcker (LKP) equation of state. The method is based on solving simultaneous equations from Plöcker's mixing rules for pseudocritical parameters of a mixture and the Lee–Kesler equation for the saturation line. For mixtures of hydrocarbons containing from two to nine carbon atoms, the divergence between calculated and experimentally based interaction coefficients (ICs) is no more than $\pm 0.4\%$. The method is extended to mixtures of polar substances. For polar mixtures, an *effective molar composition* concept is introduced which takes into account the impact of dipole moments on the process of molecular associations. Formulas for finding the effective molar composition of mixtures containing polar and/or nonpolar constituents and the binary interaction coefficient (κ_{ij}) based on this effective composition and pure component properties are shown. Calculated κ_{ij} values for 12 binary mixtures of polar substances differ by 0.4% or less from corresponding κ_{ij} values obtained by processing experimental data on saturated pressure (P_s) and saturated temperature (T_s) lines for these same mixtures. A simplified alternative κ_{ij} approximation method with an error (2–5%) is also given for mixtures of polar substances.

KEY WORDS: computer algorithm; binary interaction coefficient; equation of state; mixture; nonpolar and polar substances; thermodynamic properties; reduced properties.

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1. INTRODUCTION

In 1975, Lee and Kesler [1] proposed an equation of state for pure nonpolar substances and described mixing rules for calculating pressure–volume–temperature (p–v–t) and thermodynamic properties of mixtures, but binary interaction coefficients were not mentioned in that original work. In order to calculate the pseudocritical temperature of mixtures, the authors proposed the well-known equation

$$T_{c_{\mathrm{mix}}} = (1/V_{c_{\mathrm{mix}}}) \sum_{ij} \chi_i \chi_j V_{cij} T_{cij} \tag{1}$$

where $T_{c_{\mathrm{mix}}}$ is the pseudocritical temperature of a mixture in K; $V_{c_{\mathrm{mix}}} = \sum_{ij} \chi_i \chi_j V_{cij}$ is the pseudocritical molar volume of a mixture in $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; $V_{cij} = (\frac{1}{8})(V_{ci}^{1/3} + V_{cj}^{1/3})^3$; $T_{cij} = (T_{ci} T_{cj})^{1/2} \kappa_{ij}$; V_{ci} and V_{cj} are critical molar volumes of components i and j correspondingly in $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$; T_{ci} and T_{cj} are critical temperatures of components i and j, respectively, in K; χ_i and χ_j are molar fractions of components i and j correspondingly; and κ_{ij} equals one.

In 1978, Plöcker et al. [2] extended this work by publishing work applying the Lee and Kesler equation of state to phase equilibrium analysis in mixtures of nonpolar substances with a considerable difference in critical parameters. For this purpose the authors established that Eq. (1) did not agree with the experimental data, and they offered another formula for the pseudocritical temperature of a mixture:

$$T'_{c_{\mathrm{mix}}} = \left(\frac{1}{V^{\eta}_{c_{\mathrm{mix}}}}\right) \sum_{ij} \chi_i \chi_j V^{\eta}_{cij} T'_{cij} \tag{2}$$

where $T'_{cij} = (T_{ci}, T_{cj})^{1/2} \cdot \kappa_{ij0.25}$, $\kappa_{ij0.25}$ is the LKP binary interaction coefficient (IC) that does not depend on composition, pressure, or temperature, $\kappa_{ij0.25} = \kappa_{ij}$ if $\eta = 0.25$, and η is an empirical coefficient. The authors assigned a universal numerical value of 0.25 to η, which was obtained by processing experimental data. The $\kappa_{ij0.25}$ was considered to be a fitting parameter determined by processing experimental data exclusively. Numerical values of $\kappa_{ij0.25}$ were calculated by the authors for approximately 100 binary combinations of nonpolar components, and an empirical correlation of these κ_{ij}'s for mixtures of hydrocarbons was established as a function of the parameter $(V_{ci} T_{ci})/(V_{cj} T_{cj})$. Henceforth, whenever the Lee and Kesler (LK) equation of state was used for mixture analysis, the mixing rule indicated by Eq. (2) and κ_{ij}'s determined by processing available experimental data have been used for the thermodynamic property calculations.

In this manner the main advantage of the LK equation, which is the ability to calculate properties of mixtures using only the critical parameters of pure components, was compromised. The original LK equation afforded the opportunity to calculate the thermodynamic properties of new substances, because critical parameters could be estimated by group-contribution methods from a structural formula. A number of unsuccessful attempts were made to restore this advantage by predicting $\kappa_{ij0.25}$ from component parameters [3]. This lack of success is not surprising, because $\kappa_{ij0.25}$ is a unique fitting parameter that depends not only on properties of components but also on the extent to which the LK equation [and the models of Benedict–Webb–Rubin (BWR) and Pitzer relation that are built in] correspond to the physical nature of substances and their mixtures [4, 5]. It is necessary to remember that the basic BWR equation was developed for natural gas property analysis, and the Pitzer relation is good only for nonpolar substances like hydrocarbons. Meanwhile, the LK equation has come to be broadly used for various substances and their mixtures including polar substances.

Additionally, the optimal values of $\kappa_{ij0.25}$ differ for different thermophysical properties, and various authors optimize $\kappa_{ij0.25}$ by means of different minimization functions working with different properties [6]. As a result, the set of $\kappa_{ij0.25}$ values reported in the literature is badly generalized and shows a large range of variability. It is understandable that $\kappa_{ij0.25}$ values obtained by different authors for the same mixture differ considerably (Table I) [6]. So for nonpolar and polar mixtures, the

Table I. Variations in Lee–Kesler–Plöcker Interaction Coefficient from Experimental Data [6]

Mixture	Author	$\kappa_{ij}(x, y)$	$\kappa_{ij}(V_L)$	$\kappa_{ij}(C_p)$
R-22/R-114	Hackstein	0.963	—	—
	Kruse	0.975	0.975	—
	Ström	0.979	1.042	—
	Valtz	0.973	0.973	—
	Radermacher	—	—	0.97
R-22/R-142b	Lavue	0.993	0.997	—
	Ström	1.005	1.096	—
	Valtz	1.000	1.046	—
	Kruse	—	1.038	—
	Radermacher	—	—	1.04
R-22/R-152a	Lavue	1.013		—
	Ström	1.014		—
	Kruse	—		—
	Radermacher	—		1.02

development of an analytical method intended for predicting κ_{ij} values only on the basis of mixture component parameters is still a very compelling problem; in this article, the problem is solved for mixtures of nonpolar and polar substances.

Since the Lee–Kesler–Plöcker (LKP) equation of state was developed for nonpolar substances exclusively, a number of additional problems arise if this equation is used to evaluate properties of polar substances and their mixtures [2, 7]. The equation does not include any analytical dependencies which would account for molecular association and induced polarity. Therefore, the role of a unique binary interaction coefficient (κ_{ij}) over a complete range of concentrations becomes very complicated.

The principal significance of κ_{ij} is that it compensates for the difference between the measured experimental properties and the calculated properties of a mixture when the basic LKP equation of state is used with the accepted mixing rules for pseudocritical parameter evaluation. In the case of nonpolar mixture analysis, the binary interaction coefficient κ_{ij} compensates for two effects:

(1) the change by Plöcker et al. of the analytical structure of the $T_{c_{mix}}$ formula compared with the structure accepted in the original LK equation [2, 3] and

(2) the influence of critical parameter differences of mixture components on the $T_{c_{mix}}$ value.

The algorithm developed for nonpolar mixtures was modified so that these effects as well as effects caused by substance polarity have been taken into account.

2. INTERACTION COEFFICIENTS FOR MIXTURES OF NONPOLAR SUBSTANCES

2.1. Method of Calculation

In this work an attempt is made to predict the $\kappa_{ij0.25}$ values analytically, to develop a fundamentally grounded method for the $\kappa_{ij0.25}$ value prediction, and to estimate the importance of factors that impact the accuracy of the prediction. The most simple assumption that makes it possible to obtain the $\kappa_{ij0.25}$ value is

$$T_{c_{mix}} = T'_{c_{mix}} \tag{3}$$

From this expression we have to find different values of $\kappa_{ij0.25}$ for each value of molar concentration, χ, and then to average them. Table II

Table II. Comparison to Experimental to Calculated Lee–Kesler–Plöcker Interaction Coefficients Using Eq. (3)

	Mixture						
κ_{ij}	Ethane & propane (C_2, C_3)	Ethane & *n*-butane (C_2, C_4)	Ethane & *n*-pentane (C_2, C_5)	Ethane & *n*-hexane (C_2, C_6)	Ethane & *n*-heptane (C_2, C_7)	Ethane & *n*-octane (C_2, C_8)	Ethane & *n*-nonane (C_2, C_9)
$\kappa_{ij\text{exp.}}$	1.01	1.029	1.064	1.106	1.143	1.165	1.214
$\kappa_{ij\text{calc.}}$	1.0113	1.0333	1.0605	1.0873	1.1147	1.1417	1.1676

presents the $\kappa_{ij0.25\text{exp.}}$ values from Ref. 2 and the $\kappa_{ij0.25\text{calc.}}$ values found from Eq. (3); the formula used for averaging is

$$\kappa_{ij0.25\,\text{calc}} = \left(\sum_{\chi=0.1}^{0.9} \kappa_{ij} + 2\right) \Big/ 11 \tag{4}$$

κ_{ij} values were determined over a range of molar compositions from 0.1 to 0.9 in 0.1 increments; the sum of values obtained was increased by two because $\kappa_{ij0.25} = 1$ when $\chi = 0$, and $\chi = 1.0$. Table II shows that the calculated values track the experimental values well but, naturally, differ from them, because Eq. (1) is not sufficiently accurate when mixtures of substances with large differences in critical parameters are encountered. It is evident that the multiplier, κ_{ij}, needed for T_{cij} in Eq. (1) differs more from 1.0 with greater differences in critical parameters of mixture components. The equations given in Ref. 1 were used to find the value of the multiplier. Mixing rules of the pseudocritical parameters for a binary mixture assume the form

$$T_{c_{\text{mix}}} = \frac{\chi_1^2 V_{c1} T_{c1} + \chi_2^2 V_{c2} T_{c2} + 0.25\chi_1\chi_2(V_{c1}^{1/3} + V_{c2}^{1/3})^3 \sqrt{T_{c1} T_{c2}} \cdot \kappa_{ij1.0}}{\chi_1^2 V_{c1} + \chi_2^2 V_{c2} + 0.25\chi_1\chi_2(V_{c1}^{1/3} + V_{c2}^{1/3})^3} \tag{5}$$

$$V_{c_{\text{mix}}} = \chi_1^2 V_{c1} + \chi_2^2 V_{c2} + 0.25\chi_1\chi_2(V_{c1}^{1/3} + V_{c2}^{1/3})^3 \tag{6}$$

$$\omega_{\text{mix}} = \chi_1\omega_1 + \chi_2\omega_2 \tag{7}$$

$$Z_{c_{\text{mix}}} = 0.2905 - 0.085\omega_{\text{mix}} \tag{8}$$

$$\omega = \frac{\ln P_{\text{br}}^{\text{s}} - 5.92714 + 6.09648/T_{\text{br}} + 1.28862 \ln T_{\text{br}} - 0.169347 T_{\text{br}}^6}{15.2518 - 15.6875/T_{\text{br}} - 13.4721 \ln T_{\text{br}} + 0.43577 T_{\text{br}}^6} \tag{9}$$

where $P_{\text{br}}^{\text{s}} = 1/P_{\text{c}}$, in atm; P_{c} is the critical pressure in atm; $T_{\text{br}} = T_{\text{b}}/T_{\text{c}}$; T_{b} is the saturation temperature in K, at 1 atm of pressure; ω is the acentric factor; $Z_{c_{\text{mix}}}$ is the pseudocritical compressibility factor of the mixture; and $\kappa_{ij1.0} = \kappa_{ij}$ if $\eta = 1.0$.

The numerical constants in Eqs. (8) and (9), and, therefore, for the A and B constants below, are empirical values obtained by Pitzer, Lee, and Kesler from fitting larger amounts of property data [2, 5]. Then since $\ln P^{s}_{br} = \ln(1) - \ln P_c = -\ln P_c$, the following simplifying substitutions can be used:

$$A = 15.2518 - 15.6875/T_{br} - 13.4721 \ln(T_{br}) + 0.43577 T^{6}_{br}$$

$$B = -5.92714 + 6.09648/T_{br} + 1.28862 \ln(T_{br}) - 0.169347 T^{6}_{br}$$

with Eqs. (7) and (9) to obtain Eq. (10).

$$P_{c_{mix}} = \frac{P_{c1}^{\chi_1 A_{mix}/A_1} \cdot P_{c2}^{\chi_2 A_{mix}/A_2}}{e^{\chi_1 B_1 A_{mix}/A_1 + \chi_2 B_2 A_{mix}/A_2 - B_{mix}}} \tag{10}$$

where $P_{c_{mix}}$ is the pseudocritical pressure of a mixture in atm; $A_{mix} = f_1[(T_b/T_c)_{mix}]$ for a mixture; $B_{mix} = f_2[(T_b/T_c)_{mix}]$ for a mixture; $A_1 = f_1[(T_b/T_c)_1]$ for a component 1; $A_2 = f_1[(T_b/T_c)_2]$ for a component 2; $B_1 = f_2[(T_b/T_c)_1]$ for a component 1; $B_2 = f_2[(T_b/T_c)_2]$ for a component 2; $(T_b/T_c)_{mix}$ is the pseudoparameter of a mixture; and the functions of f_1 and f_2 are those shown for A and B above. Equation (10) fits the hypothesis that the LK equation is based on: that a mixture is a pseudosubstance. By substituting Eqs. (6), (8), and (10) into the rearranged generalized real-gas law Eq. (11), shown below, a new, independent representation of $T_{c_{mix}}$ can be obtained:

$$T_{c_{mix}} = \frac{P_{c_{mix}} V_{c_{mix}}}{R Z_{c_{mix}}} \tag{11}$$

where $R = 82.04$ (gas law constant; $\text{atm} \cdot \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

If Eq. (11) is set equal to Eq. (5), an equation with two unknowns, $(T_b/T_c)_{mix}$ and $\kappa_{ij1.0}$, results. The dependence of $(T_b/T_c)_{mix}$ on χ is defined by the change of two parameters, $T_{c_{mix}}$ and $T_{b_{mix}}$; both are pseudoparameters. The dependence of $T_{c_{mix}}$ on molar composition is given by Eq. (5); an equation similar to Eq. (5) can be written for the pseudoparameter $T_{b_{mix}}$:

$$T_{b_{mix}} = \frac{\chi_1^2 V_{c1} T_{b1} + \chi_2^2 V_{c2} T_{b2} + 0.25 \chi_1 \chi_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \sqrt{T_{b1} T_{b2}} \cdot \kappa_{ijb}}{\chi_1^2 V_{c1} + \chi_2^2 V_{c2} + 0.25 \chi_1 \chi_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3} \tag{12}$$

where $\kappa_{ijb} = 1/\kappa_{ij1.0}$ and T_{b1} and T_{b2} are normal boiling temperatures of components 1 and 2. Setting Eq. (11) equal to Eq. (5) and using Eq. (12) will result in an equation with only one unknown, $\kappa_{ij1.0}$. These $\kappa_{ij1.0}$ values can be used to calculate the $\kappa_{ij0.25}$ values by setting Eq. (11) [or Eq. (5)] equal to Eq. (2) for each value of χ and averaging the results in accordance with Eq. (4).

2.2. Nonpolar Interaction Coefficient Results

In Fig. 1, the $\kappa_{ij0.25\mathrm{exp}}$ values are presented, which have been obtained by processing experimental data for mixtures of hydrocarbons containing components with two to nine carbon atoms in their structure [2], and the $\kappa_{ij0.25\mathrm{calc}}$ values obtained by the method described above. When the $\kappa_{ij0.25\mathrm{calc}}$ values were obtained, Eq. (8) was used to determine $Z_{c_{\mathrm{mix}}}$. For some mixtures, the experimental data show values that differ slightly from calculated values. This can be explained with the help of Fig. 2. This figure shows that the actual Z_c values of components (and, consequently, $Z_{c_{\mathrm{mix}}}$) are sometimes different from the values obtained from Eq. (8).

The maximum divergence between the calculated and the experimental κ_{ij} values (that is % $\kappa_{ij\mathrm{calc}}$) was approximately ±0.4%, which may be considered quite satisfactory (see Fig. 1).

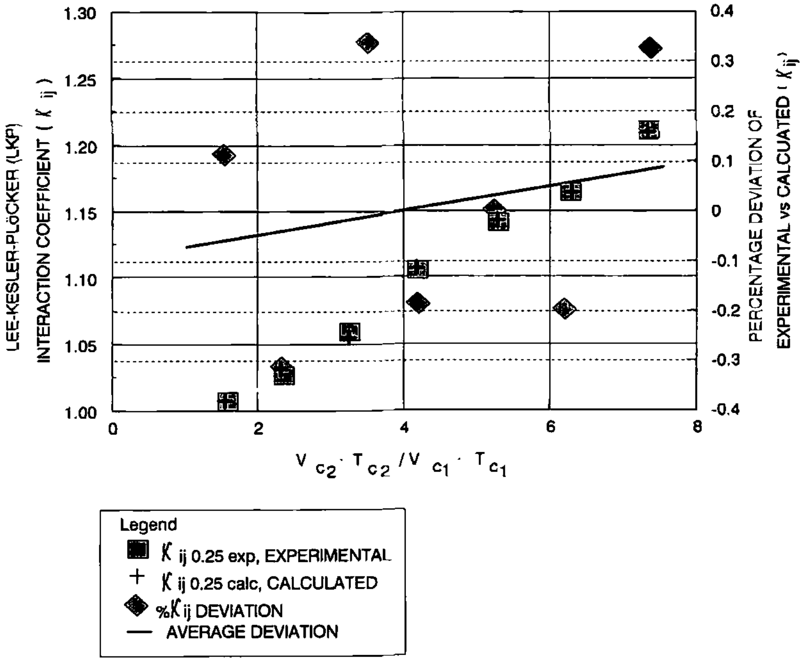

Fig. 1. Comparison of experimental with calculated interaction coefficients for mixtures of ethane with longer, straight-chain alkanes through *n*-nonane, and relative deviation of experimental versus calculated κ_{ij}'s.

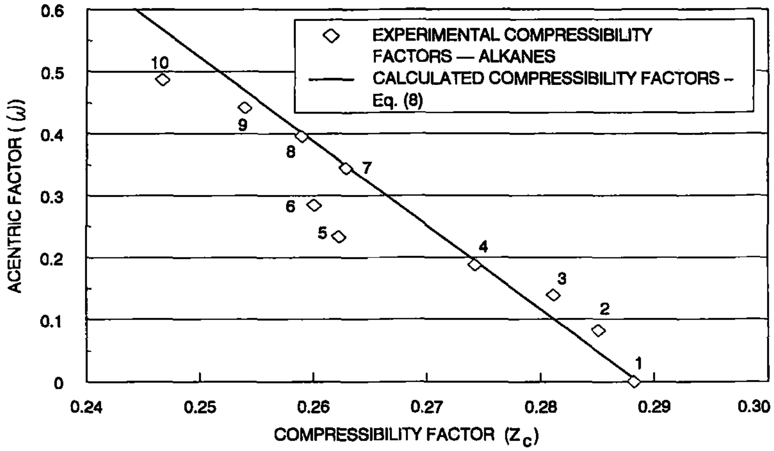

Fig. 2. Experimental and calculated compressibility factors, Z_c, obtained from Eq. (8), plotted against the acentric factor, ω, for methane (1) through n-decane (10).

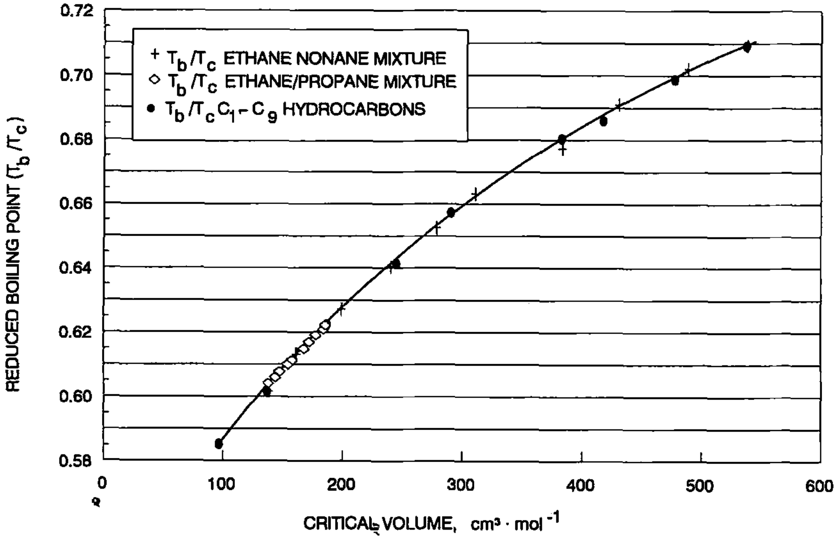

Fig. 3. The reduced boiling temperature, T_b/T_c, of pure substances C_1–C_9 and the reduced pseudo-boiling temperature, $(T_b/T_c)_{mix}$, for mixtures of ethane/nonane and ethane/propane plotted against critical volumes (V_c, $V_{c_{mix}}$).

In Fig. 3 changes in the calculated $(T_b/T_c)_{mix}$ values are plotted against the pseudocritical volume of the mixture, $V_{c_{mix}}$, for ethane–propane and ethane–nonane mixtures. The change of the (T_b/T_c) value against the mixture V_c for pure hydrocarbons C_1–C_9 is also shown. The functions almost coincide, which confirms the validity of the hypothesis describing a mixture as a pseudosubstance.

3. INTERACTION COEFFICIENTS FOR MIXTURES OF POLAR SUSBSTANCES

3.1. Method of Calculation

In order to modify the algorithm for polar substances, it was necessary to estimate how the pseudoparameter $(T_b/T_c)_{mix}$ varies for mixtures with polar constituents. Initially, it was informative to see how polarity influences the function $T_b/T_c = f(V_c)$ for *pure* polar substances. To provide for a logical organization of data, a concept of homologous groups of CFC-like substances is employed. The diagram shown in Fig. 4a illustrates the homologous groups formed by substitution of fluorine and chlorine atoms for hydrogen atoms on a methane base. The diagram in Fig. 4b displays the same principle for substances formed from ethane. In accordance with homologous principles of physical chemistry, similar sections or groups of compounds are chosen parallel to the CCl_4–CF_4 side of the methane diagram and parallel to the C_2Cl_6–C_2F_6 side of the diagram for ethane derivatives. There are other principles for dividing these substances into homologous sets, but the method chosen for this analysis is well supported by plots of the critical temperature T_c and the normal boiling temperature T_b against ordinal numbers of homologs (Fig. 5). The regular change of these parameters against the progression of homologs is a reassuring indication of homologous behavior.

The concept of homologous groups was used to build a function $T_b/T_c = f(V_c)$. These plots are presented in Fig. 6. For comparison, the function of $T_b/T_c = f(V_c)$ for homologs of the hydrocarbon series, C_1–C_{10} (nonpolar substances), is also plotted in Fig. 6. These plots indicate that the function $T_b/T_c = f(V_c)$ for nonpolar substances is a unique, smooth, continuous curve, while similar functions for polar substances are individualized for each homologous group. The value of $(T_b/T_c)_{mix}$ changes with mixture composition and will be in a range between T_b/T_c values of the individual components. It follows that, for mixtures of polar compounds from different homologous groups, the change of $(T_b/T_c)_{mix}$ will have much more complicated behavior than the corresponding function for nonpolar substances. Mixtures of R-22/R-23, R-22/R-114,

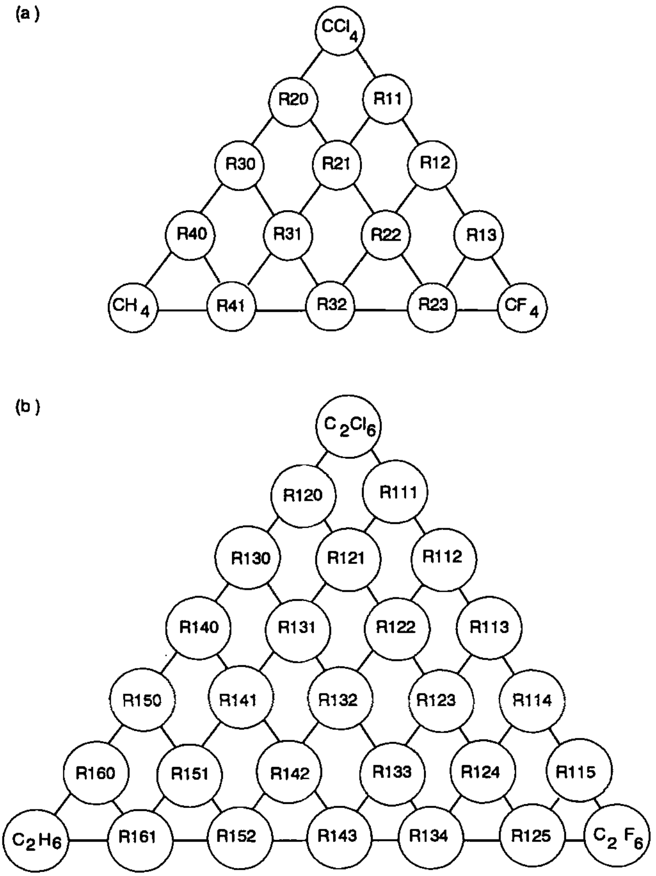

Fig. 4. Diagram of the chlorofluorocarbon (CFC) homologous groups: (a) based on methane; (b) based on ethane.

R-22/R-142b, and R-22/R-152a were chosen as references for this study. The variations of the pseudoparameter $(T_b/T_c)_{mix}$ against $V_{c_{mix}}$, that is, against changing composition, are presented in Fig. 7 for these blends. Unlike the nonpolar hydrocarbons, for which increases in the V_c values were followed by increases in T_b/T_c, the polar substances showed two regions of dependence: direct dependence when $(T_b/T_c)_{mix}$ rises with an increase in $V_{c_{mix}}$ and inverse dependence when $(T_b/T_c)_{mix}$ decreases with increasing $V_{c_{mix}}$. So if the modified interaction coefficient algorithm contains the same formulae of $T_{b_{mix}}$ and $T_{c_{mix}}$ that were used previously, in some cases it will give $(T_b/T_c)_{mix}$ values which correspond to the first region, while in other cases it will give the inverse relation.

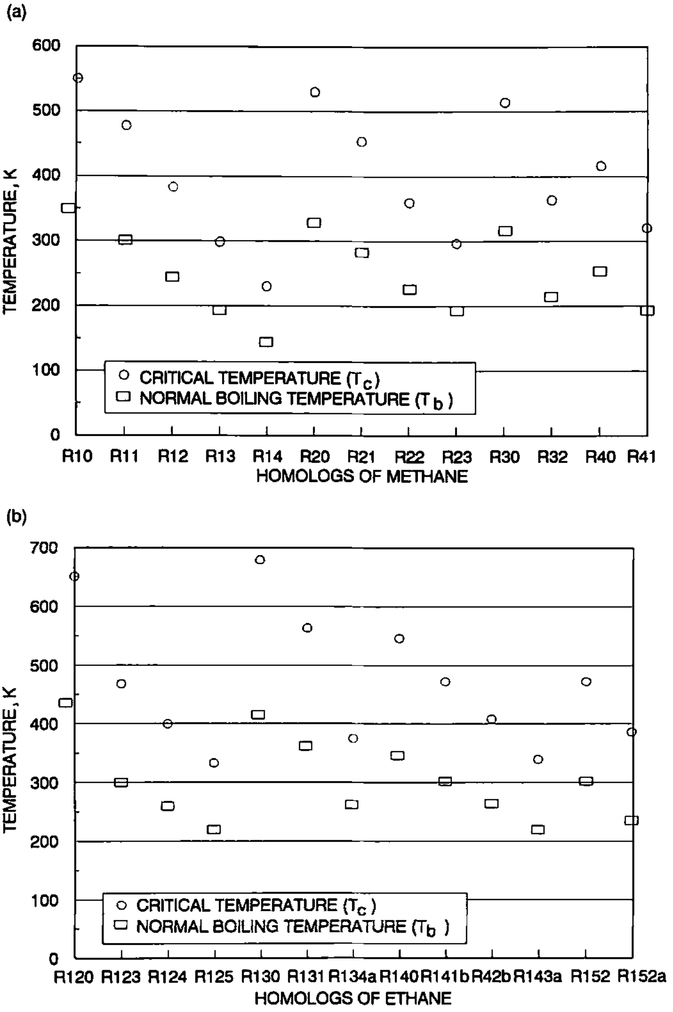

Fig. 5. The critical temperatures, T_c, and normal boiling temperatures, T_b, of compounds forming CFC homologous groups: (a) based on methane; (b) based on ethane.

Equation (8) does not result in realistic values of $Z_{c_{mix}}$ in all cases. In Fig. 8, the Z_{ci} values calculated by that equation for polar substances and experimental values of Z_{ci} are plotted against ω. Obviously, the calculated values of $Z_{c_{mix}}$ resulting from Eq. (8), which relies on a linear interpolation of ω, do not coincide with the $Z_{c_{mix}}$ values obtained by direct interpolation between the actual Z_{ci} values of components. Stated differently, the use of

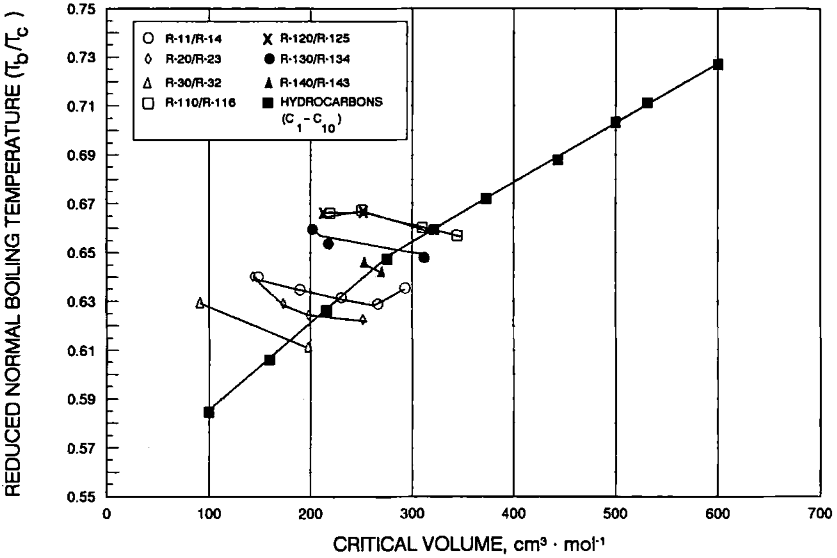

Fig. 6. Values of the reduced normal boiling temperature, T_b/T_c, plotted against critical molar volumes for polar and nonpolar compounds.

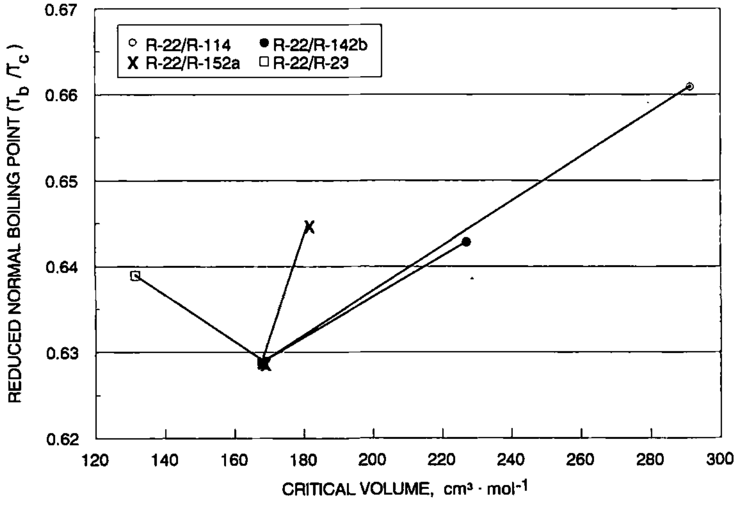

Fig. 7. Changes in the value of $(T_b/T_c)_{mix}$ plotted versus $V_{c_{mix}}$ for CFC mixtures.

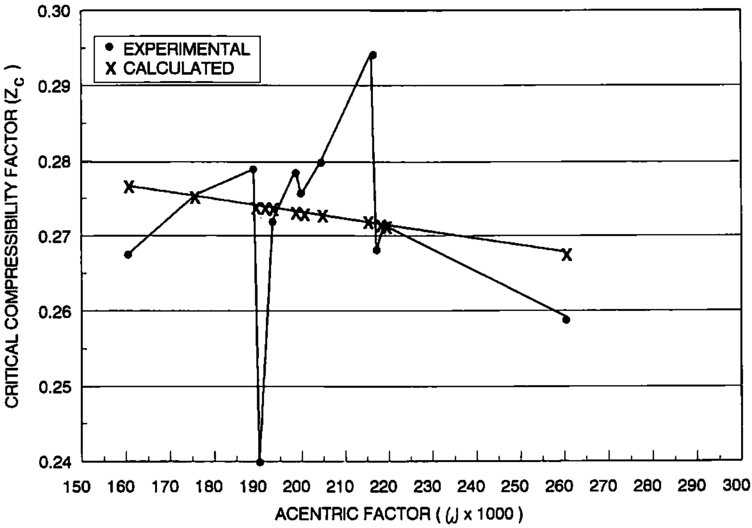

Fig. 8. Values of the critical compressibility factor, Z_c, and the calculated compressibility factor, $Z_{c_{calc}}$, obtained from Eq. (8) plotted against the acentric factor for CFC refrigerants.

the interaction coefficient estimating algorithm used for mixtures containing nonpolar components will not provide values of κ_{ij} that agree well with those calculated from experimental data for polar mixtures. The algorithm does not take into account the influence of component polarity upon the mutual association of molecules.

To modify the algorithm and to adjust it to mixtures of polar substances, a concept of *effective molar composition* of polar mixtures is introduced. The effective molar composition is defined with the help of the following equations:

$$\chi_{1ef} = x_1 \frac{(1+d_1)^q}{x_1(1+d_1)^q + x_2(1+d_2)^q} \tag{13}$$

$$\chi_{2ef} = x_2 \frac{(1+d_2)^q}{x_1(1+d_1)^q + x_2(1+d_2)^q} \tag{14}$$

where χ_1 and χ_2 are mole fractions of components; χ_{1ef} and χ_{2ef} are effective mole fractions of components that take into account influence of polarity upon mixture characteristics; $d_1 = 10^5 D_1^2 P_{c1}/T_{c1}^2$; and $d_2 = 10^5 D_2^2 P_{c2}/T_{c2}^2$. In the last two equations, d_1 and d_2 are nondimensional, reduced, polarity factors of mixture components, D_1 and D_2 are dipole moments of components in D, and q is an exponent which defines the influence of polarity upon changes in mixture parameters.

Equations (13) and (14) fit the following conditions.

(1) The sum of effective mole fractions of components always equals one if $\chi_1+\chi_2=1$, that is, the condition of material balance is satisfied.

(2) If $\chi_1=1$, $\chi_2=0$, then $\chi_{1\mathrm{ef}}=\chi_1=1$, and if $\chi_1=0$, $\chi_2=1$, then $\chi_{2\mathrm{ef}}=\chi_2=1$; thus the condition of passing to the limit on concentration is accomplished.

(3) If $d_1=0$, $d_2=0$, then $\chi_{1\mathrm{ef}}=\chi_1$ and $\chi_{2\mathrm{ef}}=\chi_2$. This is a limiting condition that reduces the modified algorithm to the nonpolar case, making the modified algorithm a general case with respect to the algorithm for mixtures of nonpolar substances.

(4) When $q=0$, the modified algorithm allows determination of κ_{ij} for mixtures of polar substances without taking into account characteristics of mutual influence of the molecular polarity of components.

(5) When $d_1=d_2$, the modified algorithm allows no supplementary influence upon mixture characteristics due to the polarity of mixture components; therefore mixtures of components with the same reduced polarity must be described correctly by the algorithm for nonpolar substances.

(6) When $d_1=0$ and $d_2\neq 0$, then $q\neq 0$ and the modified algorithm adjusts the concentrations for calculation of the interaction coefficients such that $(\chi_{1\mathrm{ef}})/(\chi_{2\mathrm{ef}})=(\chi_1/\chi_2)/(1+d_2)^q$. Explicit values for $\chi_{1\mathrm{ef}}$ and $\chi_{2\mathrm{ef}}$ can be calculated knowing that $\chi_{1\mathrm{ef}}+\chi_{2\mathrm{ef}}=1.00$.

The results of the analysis above have allowed development of a logical structure for a modified algorithm to determine κ_{ij} values for mixtures of nonpolar, polar/nonpolar, and polar substances. The algorithm consists of three stages. In the first stage, when $q=0$, the $\kappa^0_{ij1.0}$ value is determined, that is, the value of $\kappa_{ij1.0}$ from Eq. (5) with exponent η for $V_{\mathrm{c}1}$, $V_{\mathrm{c}2}$, and $V_{\mathrm{c_{mix}}}$ equal to unity.

In the second stage, when $q\neq 0$ and $\kappa^0_{ij1.0}$ is known from the first stage, the value of $\kappa^q_{ij1.0}$ is determined by using a supplementary analytical dependence that exists between q and $\kappa^q_{ij1.0}$. This dependence is formed as follows:

$$\text{when } q=q_0=0, \qquad \kappa_{ij1.0}=\kappa^0_{ij1.0} \tag{15}$$

$$\text{when } q=q_{\mathrm{f}}, \qquad \kappa_{ij1.0}=\kappa^q_{ij1.0} \tag{16}$$

where q_f is the final value of q that corresponds to the solution, so that

$$\Delta q = q_p - q_0 = f(\kappa^0_{ij1.0} - \kappa^P_{ij1.0}) \tag{17}$$

where q_p is the current value of q and where $\kappa^P_{ij1.0}$ is the current value of $\kappa_{ij1.0}$.

Since $\kappa^P_{ij1.0}$ is centered on unity, the function Δq may be represented as a polynomial in terms of $(\kappa^0_{ij1.0} - \kappa^P_{ij1.0})$, and the expression that allows for finding the value of Δq assumes the form

$$\Delta q = A(\kappa^0_{ij1.0} - \kappa^P_{ij1.0}) + B(\kappa^0_{ij1.0} - \kappa^P_{ij1.0})^2 + \cdots \tag{18}$$

The coefficients A and B are found by the method described in Ref. 9 under the condition that if $(V_{c2}T_{c2})/(V_{c1}T_{c1}) \to 1$, then $\kappa_{ij1.0} \to 1$ and $q \to 0$; they assume the forms

$$A = \frac{d_{21}(V_cT_c)_{21}}{T^2_{c21}[1-(V_cT_c)_{21}]^2} \tag{19}$$

$$B = \frac{d^2_{21}[(V_cT_c)^2_{21} - 1]}{T^4_{c21}(V_cT_c)_{21}\,[1-(V_cT_c)_{21}]^2} \tag{20}$$

where $d_{21} = (1+d_2)/(1+d_1)$, $T_{c21} = T_{c2}/T_{c1}$, and $(V_cT_c)_{21} = (V_{c2}T_{c2})/(V_{c1}T_{c1})$.

With Eqs. (13)–(20) the second stage of the algorithm is reduced to the $\kappa^q_{ij1.0}$ evaluation from the algorithm for mixtures of nonpolar substances by implementing effective molar compositions instead of actual molar compositions in Eq. (11). The solution is found by the method of successive approximations.

In the third stage the $\kappa_{ij0.25}$ values needed for LKP calculations are found similarly to the method used for mixtures containing nonpolar components with the substitution of $\kappa^q_{ij1.0}$ for $\kappa_{ij1.0}$.

3.2. Polar Interaction Coefficient Results

Twelve reference mixtures were used for the investigation and estimation of the proposed algorithm. Table III lists the basic physical property data of the mixture components, and Table IV contains a list of mixtures and their dimensionless characteristics.

The equations used in the algorithm are, in principle, not dependent on the sequence in which mixture components are selected. However, the data in Table IV are arranged in order of increasing dipole moments, $D_2/D_1 > 1$, and with all the mixtures listed in decreasing order of the parameter $(V_{c2}T_{c2})/(V_{c1}T_{c1})$ values.

Table III. Basic Physical Properties of Mixture Components

Component	M	T_b (K)	T_c (K)	P_c (MPa)	V_c ($cm^3 \cdot mol^{-1}$)	D (D)
1. R-22	86.470	232.288	369.300	5.0540	168.986	1.458
2. R-23	70.010	191.120	299.100	4.900	132.8211	1.650
3. R-32	52.020	221.500	351.360	5.791	120.00	1.98
4. R-114	170.92	276.799	418.800	3.248	307.023	0.96
5. R-124	136.480	259.960	395.620	3.637	243.801	1.469
6. R-134	102.03	253.340	392.100	4.562	189.014	1.20
7. R-134a	102.030	247.00	374.300	4.067	199.05	2.058
8. R-142b	100.500	264.010	410.290	4.120	230.981	2.14
9. R-152a	66.050	248.500	386.700	4.492	181.011	2.27

The calculated values of $\kappa^0_{ij0.25}$ when $q = 0$, and the experimental values of $\kappa_{ij0.25}$ are plotted against $V_{c2}T_{c2}/V_{c1}T_{c1}$ in Fig. 9. This plot indicates how poorly the algorithm developed for calculating the interaction coefficients for nonpolar mixtures fits the data for mixtures on polar refrigerants. The $\kappa_{ij\text{exp.}}$ values were obtained by processing experimental data for saturated pressures and saturated temperatures taken from condensation and evaporation lines of mixtures [3, 10–18]. With the help of the LKP equation, the $\kappa_{ij\text{exp.}}$ values were determined by minimizing the deviations of calculated values for saturated pressure and temperature from the experimental values [4].

Table IV. Basic Data on Mixture Characteristic Parameters

Number	Mixture components	T_{c2}/T_{c1}	$V_{c2}T_{c2}/V_{c1}T_{c1}$	Dipole moment ratio	Reduced polarity factor
1	R-23/R-134a	1.2514	1.875	1.2473	0.8245
2	R-32/R-134a	1.0653	1.7667	1.0394	0.6686
3	R-22/R-124	1.0713	1.5456	1.0075	0.6366
4	R-22/R-142b	1.111	1.5186	1.4678	1.4228
5	R-22/R-152a	1.0471	1.1216	1.5569	1.965
6	R-134/R-134a	0.9546	1.0051	1.715	2.8774
7	R-134/R-152a	0.9862	0.9445	1.8917	3.6226
8	R-124b/R-134a	0.9461	0.7723	1.401	2.4519
9	R-124/R-152a	0.9725	0.7257	1.5453	3.0862
10	R-22/R-23	0.8099	0.6366	1.1317	1.8930
11	R-114/R-22	0.8818	0.4853	1.5187	4.6158
12	R-114/R-23	0.2142	0.3090	1.7188	8.7375

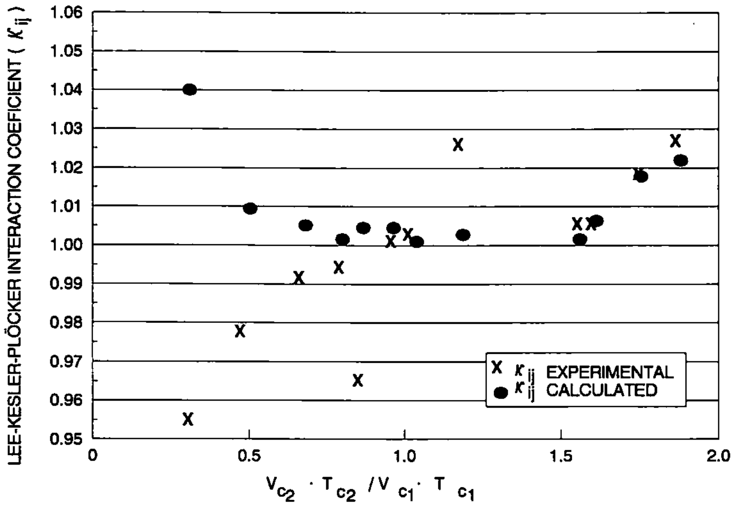

Fig. 9. Values of the experimental interaction coefficient, $\kappa_{ij0.25\mathrm{exp}}$, and values calculated without considering polarity, $\kappa_{ij0.25\mathrm{calc}}$, plotted against the parameter $(V_{c2}T_{c2})/(V_{c1}T_{c1})$.

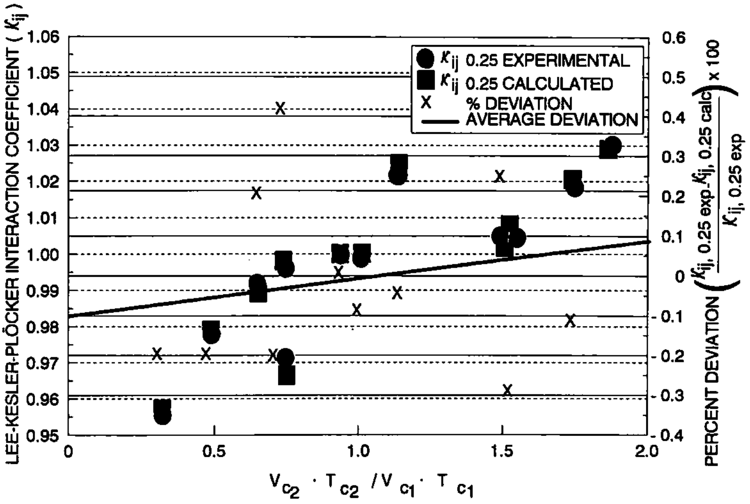

Fig. 10. Values of the experimental interaction coefficient, $\kappa_{ij0.25\mathrm{exp}}$, calculated interaction coefficient, $\kappa_{ij0.25\mathrm{calc}}$, and % κ_{ij} deviation plotted against the parameter $(V_{c2}T_{c2})/(V_{c1}T_{c1})$.

Joint examination of Fig. 9 and Eq. (18) leads to the following:

$$\kappa_{ij} > 1, \qquad q < 0, \qquad \text{if} \quad V_{c2} T_{c2} / V_{c1} T_{c1} > 1 \tag{21}$$

$$\kappa_{ij} < 1, \qquad q > 0, \qquad \text{if} \quad V_{c2} T_{c2} / V_{c1} T_{c1} < 1 \tag{22}$$

In order for the proposed algorithm to conform to the actual physical nature of the system, calculation results should correspond to these relations. A computer code has been developed for determining κ_{ij} from the proposed algorithm. An iterative process is used to obtain the results.

The values of κ_{ij}'s determined from experimental data and those obtained from the proposed algorithm for all 12 reference mixtures are presented in Fig. 10. The percentage deviation between experimental and calculated values never exceeds ±0.4%. It is necessary to emphasize that the calculation of κ_{ij} with the help of the proposed algorithm has been performed *without* using any *experimental* data on mixtures. Only pure-component physical property data were used.

If only a rough approximation is required for the κ_{ij} value, the following approximation equation is offered:

$$\kappa_{ij\mathrm{ap}} = \kappa_{ij[13]} + (0.016 - 0.0012 d_{21})(V_c T_c)_{21} \tag{23}$$

Equation (23) has been obtained by including parameters indicative of polarity into an approximation equation found in Ref. 13; $\kappa_{ij[13]}$ is the value obtained from the formula in this reference. The error of the κ_{ij} calculations when Eq. (23) is applied reaches (2–5)%.

4. CONCLUSIONS

The method outlined above makes it possible to obtain binary interaction coefficients values, κ_{ij}, for the LK equations of state with a maximum deviation of 0.4% using the critical parameters of mixture components and their normal boiling temperatures, T_b. The method does not have any restrictions imposed by the nature of the components and may be recommended as a general method for calculating the κ_{ij} values when the LK equation of state is applied to mixtures of both nonpolar and polar substances.

The algorithm developed allows examining mixtures of polar substances in the scope of assumptions made for the LKP equation of state using component property data exclusively. This algorithm gives the LK equation an advantage it originally had over other equations of state, the ability to make thermodynamic property calculations with a bare minimum of experimental property information. The required input data for each component are molecular weight (M), critical pressure (P_c), critical temperature (T_c), normal boiling temperature (T_b), critical volume (V_c), and dipole moment (D). All these values may be estimated using only the chemical structure of a substance, if necessary [8].

So the LKP equation of state together with the developed algorithm for the determination of κ_{ij} may be used for predicting properties of mixtures of new or even nonexistent substances, in which case the substance structure is used to estimate required information. In this way, it is possible initially to screen the thermodynamic performance characteristics of new substances for energy cycles and cycles in refrigeration or air-conditioning equipment.

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