

Article

Elements and Chemical Bonds Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures

Haodong Liu ¹, Xinyu Li ¹, Yuxin Wang ¹, Xiaoyan Sun ¹, Wenying Zhao ², Li Xia ^{1,*} and Shuguang Xiang ^{1,*}

¹ Institute of Process System Engineering, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

² College of Chemistry and Chemical Engineering, Qilu Normal University, Jinan 250200, China

* Correspondence: xiali@qust.edu.cn (L.X.); xsg@qust.edu.cn (S.X.)

Abstract: Based on the contribution of elements and chemical bonds, the UNICAC (Universal Quasi-Chemical elements and chemical bonds Activity Coefficient) method was proposed to estimate the activity coefficients of nonelectrolyte liquid mixtures. The UNICAC method defined 10 elements and 33 chemical bonds as contribution groups. The calculation of activity coefficients was divided into the combination term and the residual term. The combination term represents molecular size differences, and the residual term describes the interaction between molecules. The interaction energy parameters of 43 groups were regressed simultaneously with the experimental data of the vapor–liquid equilibrium of 1085 binary systems. According to the molecular structural information of compounds, the UNICAC method can accurately predict the activity coefficients of nonelectrolyte liquid mixtures. The vapor–liquid equilibrium of 16 groups of the binary system, which were not included in the parameters regress, was predicted using UNICAC. The average relative error of vapor composition was 1.53%. Compared with UNIFAC (2003), UNIFAC (Lyngby), UNIFAC (Dortmund), and ASOG (2011), the UNICAC model employs fewer parameters, provides a broader scope of application, and receives more precise predicted results of the vapor–liquid equilibrium. The UNICAC method would play an important reference role in the design of the chemical separation process.

Keywords: elements; chemical bonds; vapor–liquid equilibrium; activity coefficient; group contribution



Citation: Liu, H.; Li, X.; Wang, Y.; Sun, X.; Zhao, W.; Xia, L.; Xiang, S. Elements and Chemical Bonds Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *Processes* **2022**, *10*, 2141. <https://doi.org/10.3390/pr10102141>

Academic Editor: Jui-Yuan Lee

Received: 21 September 2022

Accepted: 12 October 2022

Published: 20 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Products, process, and separation engineering design need complex fluids vapor–liquid equilibrium (VLE) data [1]. It can be determined with an experimental method. However, the experimental methods may be restricted by the experimental conditions, and they will consume a lot of human and material resources [2]. The vapor–liquid equilibrium data can also be predicted using phase equilibrium mathematical models based on the group contribution method and thermodynamic property prediction software based on molecular descriptors. Nowadays, the use of molecular descriptors to predict row phase equilibria is a new trend in the era of big data, and they have greatly improved in computational efficiency and convenience. Commercial software such as the COSMO-SAC model is available. As thermodynamic property prediction software also relies primarily on reliable mathematical models, developing and improving the underlying models are essential for thermodynamic property prediction. In terms of the group contribution method, the fugacity coefficient of vapor phases was usually calculated with an equation of state, and the activity coefficient of liquid phases was calculated with activity coefficient models [3].

The earliest activity coefficient models such as the Wohl, Margules and van Laar equations use ‘average’ or ‘overall’ compositions, and their theoretical basis is ‘random mixing’. However, due to intermolecular forces, the mixing of molecules is never entirely random. The models could be improved, considering the non-randomness, leading to better descriptions of phase behavior. Since the Wilson equation was proposed in 1964,

local composition (LC) activity coefficient models have drastically changed the applicability range of liquid phase models. There exist several models that employ the LC concept, such as Wilson, NRTL, and UNIQUAC [4]. Although those models can give good predictions of liquid-phase activity coefficients, they need experimental VLE data to obtain model parameters [5]. However, the required experimental data are not always available.

One of the most successful methods presently used for calculating activity coefficients of the liquid phase is the group contribution (GC) method, in which the liquid phase is considered a mixture of structural groups [6]. The first GC method for the calculation of activity coefficients was ASOG (Analytical Solution of Groups), based on the Wilson equation, but an FH (Flory–Huggins model) combinatorial term was added. The ASOG model was proposed by Deal and Derr in 1969, and then it was modified by Tochigi (1990) [7] and Gmehling (2011) [8]. Meanwhile, the group interaction parameters were supplemented, and the number of groups was up to 47. Because of the absence of necessary groups or interaction parameters, the VLEs of some systems cannot be predicted, which restricts the application of the ASOG model. To improve the situation, Robles et al. (2016) [9] added 14 group-interaction parameters for the ASOG model, such as CH_2/Imide and CH_2/PF_6 .

Another well-known GC activity coefficient model is UNIFAC (Universal quasi-chemical Functional group Activity Coefficient). The UNIFAC model was proposed by Fredenslund et al. in 1975 [10]. The group-interaction parameters table of the UNIFAC model was revised and supplemented by Fredenslund et al. (1977) [11], Jørgensen et al. (1979) [12], Gmehling et al. (1982) [13], Macedo et al. (1983) [14], Tiegs et al. (1987) [15], Hansen et al. (1991) [16], and Wittig et al. (2003) [17].

In addition to revising and complementing the parameters, the combination and residual terms were improved using the UNIFAC (Lyngby) and UNIFAC (Dortmund) modified models. The modified UNIFAC (Lyngby) model divides 21 groups [18]. Although the modified model has a high estimation accuracy, the prediction range is relatively narrow. The UNIFAC (Dortmund) modified model is widely used in chemical design and production. With the expansion of the application range, the number of main groups and the required group-interaction parameters increase. The UNIFAC (Dortmund) parameter matrix was revised five times by Gmehling et al. (1993, 1998, 2002, 2006, and 2016) [19–23].

The UNIFAC method has become very popular because of its availability on commercial process simulators, its reliably predicted phase equilibrium results, and its simple usage. The UNIFAC method has several well-known limitations, for example, the problem of missing groups or group-interaction parameters [24]. According to the newly released group-interaction parameter matrix in 2016, the number of main groups has increased from 64 to 103. It can be seen that a total of 5356 parameters are needed, 1828 are obtained, and 65.87% of the parameters are still missing [23]. Because of missing major groups or interaction parameters, the vapor–liquid equilibrium data of some systems cannot be predicted. This limits the further application of UNIFAC (Dortmund). For example, Klauck et al. (2019) [25] determined the group parameters of ammonia and the interaction parameters between groups. Qin et al. (2019) [26] obtained six binary interaction parameters between $\text{C}_2\text{H}_2\text{F}$, CF_4 , CF_3 , and CH_3 using the regression of experimental data. The VLE data of a methanol (1) + water (2) mixture from 298.15 K to 373.15 K was also regressed using the UNIFAC model by Nayak et al. (2022) [27].

In order to improve the problem of many groups and the lack of parameters in the traditional group contribution method, Xia et al. proposed the group division method based on elements and chemical bonds. Using the experimental data in the database manual of thermodynamics and the physical properties of compounds edited by Carl L. Yaws, a method based on the contribution of 10 elements and 33 chemical bonds was proposed to estimate the critical properties by Li (2016), which has high prediction accuracy [28]. The method based on the elements and chemical bonds contribution is successfully applied to estimate the properties of pure substances.

If fewer basic contribution groups are established in the GC activity coefficient model, the possibility of the group-interaction parameters missing will be less. Based on the above

ideas, the UNICAC model (Universal Quasi-Chemical elements and chemical bonds Activity Coefficient) for estimating activity coefficients based on elements and chemical bonds will be proposed. The new model uses vapor–liquid phase equilibrium data (1085 data sets and 14,323 data points) for binary systems containing 14 types of compounds and regresses the interaction energy parameters between 10 elements and 33 chemical bonds using the sum of log errors squared of the experimental and calculated values of the activity coefficients as the objective function and a fitted Newtonian method to find their minimum values. Compared to the previous functional group contribution method, the UNICAC model has a relatively more complete set of necessary groups to split the compound, and a smaller scale of group interaction parameters. It also improves the prediction accuracy of aromatic hydrocarbon ring by considering the benzene ring. The UNICAC model was compared with UNIFAC [10–17], UNIFAC (Dortmund) [19–23], UNIFAC (Lyngby) [18], and ASOG (2011) [7–9] to verify their accuracy and applicability range.

2. Method and Property Modeling

2.1. Data

The fundamental idea of the UNICAC model is to utilize the existing phase equilibrium data for predicting the phase equilibrium of systems for which no experimental data are available. The quality of the method strongly depends on the experimental data. The sources of vapor–liquid equilibrium data in this work were the literature [29]. This included alkanes, alkenes, alkynes, cycloalkanes, alcohols, ketones, esters, acids, halogenated hydrocarbons, nitrogenous compounds, etc. The data checked for thermodynamic consistency were used in this work.

2.2. Groups

The UNICAC model used elements and chemical bonds as the contribution group. The elements were divided into carbon (C), hydrogen (H), nitrogen (N), oxygen (O), silicon (Si), sulfur (S), fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). The chemical bonds were divided into two categories, cyclic and non-cyclic. We divided chemical bonds based on each chemical bond at both ends that connect different atoms to different chemical bonds, such as C–C, C–H, C–O, C–S, and O–H. The structural group H₂O describes water. According to this principle, the elements and chemical bond groups are seen in Table 1.

Table 1. The volume and surface of elements and chemical bonds.

Chemical Bonds	No.	$R_k/(\text{cm}^3 \cdot \text{mol}^{-1})$	$Q_k/(10^9 \text{ cm}^2 \cdot \text{mol}^{-1})$	Group Assignment Examples
H ₂ O	1	0.92	1.4	water: 1(1)
C	2	12.39	2.19	butane: 4(2),10(3),3(12),10(18)
H	3	4.36	1.09	ethyl alcohol: 2(2),6(3),1(4),1(12),1(15),1(17), 5(18)
O	4	8.51	1.70	methyl alcohol: 1(2),4(3),1(4), 1(15),1(17), 3(18)
N	5	9.39	1.82	propylamine: 3(2),9(3),1(5),1(15),1(17)
S	6	14.70	2.45	n-butyl mercaptan: 4(2),10(3),1(6),3(12),10(18),1(23),1(29)
F	7	8.01	1.63	perfluorobenzene: 6(2),6(7),6(19),1(37)
Cl	8	13.51	2.32	chloroform: 1(2),1(3),3(8),1(18),3(20)
Br	9	15.96	2.59	bromoethane: 2(2),5(3),1(9),1(12),5(18),1(21)
I	10	19.57	2.97	ethyl iodide: 2(2),5(3),1(10),1(12),5(18),1(22)
Si	11	23.35	3.34	silicontetrachloride: 4(8),1(11),4(25)
C–C	12	−3.86	−1.02	isopentane: 5(2),12(3),4(12),12(18)
C=C	13	−5.46	−1.24	isoprene: 5(2),8(3),2(12),2(13),8(18)
C≡C	14	−4.84	−1.34	vinylacetylene: 4(2),4(3),1(12),1(13),1(14),4(18)
C–O	15	−4.54	−1.05	propanoic acid: 3(2),6(3),2(4),2(12),1(15),1(16),1(17),5(18)
C=O	16	−4.96	−1.16	allyl acetate: 5(2),8(3),2(4),2(12),1(13),2(15),1(16),8(18)
O–H	17	−2.92	−0.80	l-hexanol: 6(2),14(3),1(4),5(12),1(15),1(17),13(18)
C–H	18	−3.35	−0.98	benzene: 6(2),6(3),6(18),1(37)
C–F	19	−4.48	−0.97	dichlorodifluoromethane: 1(2),2(7),2(8),2(19),2(20)
C–Cl	20	−3.56	−0.99	1,1-dichloroethane: 1(2),2(7),2(8),2(19),2(20)

Table 1. Cont.

Chemical Bonds	No.	$R_k/(\text{cm}^3 \cdot \text{mol}^{-1})$	$Q_k/(10^9 \text{ cm}^2 \cdot \text{mol}^{-1})$	Group Assignment Examples
C-Br	21	-3.72	-0.90	bromoform: 1(2),1(3),3(9),1(18),3(21)
C-I	22	-2.17	-1.01	methyl iodide: 1(2),3(3),1(10),3(18),1(22)
C-S	23	-4.45	-1.02	propyl mercaptan: 3(2),8(3),1(6),2(12),7(18),1(23),1(29)
C-Si	24	-5.47	-1.11	tetra-ethylsilane: 8(2),20(3),1(11),20(18),4(24)
Si-Cl	25	-4.07	-1.19	dichlorophenylsilane: 6(2),6(3),2(8),1(11),5(18),1(24),2(25),1(26),1(27)
Si-H	26	-3.70	-0.99	trichlorosilane: 1(3),3(8),1(11),3(25),1(26)
Si-O	27	-2.81	-1.28	hexamethyldisiloxane: 6(2),18(3),1(4),2(11),18(18),6(24),2(27), 1(26),1(27)
C=S	28	-0.342	-0.464	carbon disulfide: 1(2),2(6),2(28)
S-H	29	-2.05	-0.69	ethyl mercaptan: 2(2),6(3),1(6),1(12),6(18),1(23),1(29)
S=O	30	-3.19	-1.04	dimethylsulfoxide: 2(2),6(3),1(4),1(6),6(18),2(23),1(30)
C-N	31	-3.05	-0.87	diethylamine: 4(2),11(3),1(5),2(12),10(18),2(31),1(34)
C=N	32	-5.29	-1.35	methyl isocyanate: 2(2),3(3),1(4),1(5),1(16),3(18),1(31),1(32)
C≡N	33	-5.22	-1.28	methacrylonitrile: 4(2),5(3),1(5),2(12), 1(13),5(18),1(33)
N-H	34	-3.32	-0.77	aniline: 6(2),7(3),1(5),5(18),1(31),2(34),1(37)
N-O	35	-3.16	-0.82	methylethylketoxim: 4(2),9(3),1(4),1(5),3(12),1(17),8(18),1(32), 1(35)
NO ₂	36	-9.07	-2.46	nitromethane: 1(2),3(3),2(4),1(5),3(18),1(31),1(36)
benzene	37	-29.93	-7.58	toluene: 7(2),8(3),1(12),8(18),1(37)
c-C-C	38	-4.47	-1.12	cyclohexane: 6(2),12(3),12(18),6(38)
c-C=C	39	-5.53	-1.31	furan: 4(2),4(3),1(4),4(18),1(38),2(39),2(40)
c-C-O	40	-4.54	-1.03	1,4-dioxane: 4(2),8(3),2(4),8(18),2(38),4(40)
c-C-S	41	-4.02	-0.99	thiophene: 4(2),4(3),1(6),4(18),1(38),2(39),2(41)
c-C-N	42	-2.87	-0.95	morpholine: 4(2),9(3),1(4),1(5),8(18),1(34),2(38),2(40), 2(42)
c-C=N	43	-5.89	-0.79	pyridine: 5(2),5(3),1(5),5(18),2(38),2(39),1(42),1(43)

2.3. Models

The UNICAC model contains a combinatorial part, essentially due to differences in the sizes and shapes of the molecules in the mixture, and a residual part, essentially due to energy interactions. The combinatorial part of the UNIQUAC activity coefficients and the residual part of the ASOG activity coefficients are used separately. The sizes and interaction surface areas of elements and chemical bonds are introduced from independently obtained pure-component molecular structure data. The resulting UNICAC model contains two adjustable parameters per pair of elements and chemical bonds.

In a multi-component mixture, the UNICAC equation for the activity coefficient of the (molecular) component i is

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

where

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^{n_c} x_j l_j \quad (2)$$

and

$$\ln r_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (3)$$

$$\ln \Gamma_k = - \ln \sum_l X_l a_{lk} + 1 - \sum_l \frac{X_l a_{kl}}{\sum_m X_m a_{lm}} \quad (4)$$

$$X_l = \frac{\sum_i x_i v_l^i}{\sum_i x_i \sum_k v_k^i} \quad (5)$$

where Γ_k is the group residual activity coefficient, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i . In Equation (3), the

term $\Gamma_k^{(i)}$ is necessary to attain the normalization that the activity coefficient r_i becomes unity as $x_i \rightarrow 1$. The activity coefficient for group k in molecule i depends on the molecule i in which k is situated.

$$l_i = \left(\frac{z}{2}\right)(r_i - q_i) - (r_i - 1), z = 10 \quad (6)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (7)$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (8)$$

In these equations, x_i is the molar fraction of component i , and the summations in Equations (2) and (3) are overall components, including component i . θ_i is the area fraction, and ϕ_i is the segment fraction, which is similar to the volume fraction. The pure component parameters r_i and q_i are, respectively, measures of the molecular van der Waals volumes and molecular surface areas.

In the UNICAC method, the combinatorial part of the UNIQUAC activity coefficients in Equation (2) are used directly. Only pure component properties enter into this equation. Parameters r_i and q_i are calculated as the sum of the group volume and area parameters, R_k , and Q_k , which are given in Table 1:

$$r_i = \sum_k \nu_k^{(i)} R_k \quad (9)$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \quad (10)$$

In Equations (4) and (5), $\nu_k^{(i)}$, which is always an integer, is the number of groups of type k in molecule i . Group parameters R_k and Q_k are obtained from the van der Waals group volume and surface areas V_k and A_k , given by Bondi [30]:

$$R_k = V_k / 15.17 \quad (11)$$

$$Q_k = A_k / (2.5 \times 10^9) \quad (12)$$

The normalization factors 15.17 and 2.5×10^9 are those given by Abrams and Prausnitz (1975) [10].

2.4. Group Interaction Parameters

It was necessary to first calculate the activity coefficients from the database to obtain the interaction parameters between the elements and chemical bonds. Only low-pressure phase equilibrium data were used. Vapor-phase nonidealities were not taken into account. One thousand eighty-five binary data sets (14,323 data points) representing vapor–liquid equilibrium were used as the base data in this work. The parameters were fitted simultaneously using the base data, which were checked for thermodynamic consistency.

The objective function, which is minimized by the parameter estimation program in the software MATLAB, is a sum of the squared deviations between the experimental and calculated activity coefficients. The deviations are normalized relative to a preset standard deviation (10^{-6}), and the resulting expression for the objective function is then

$$F = \sum_{k=1}^S \sum_{j=1}^N \sum_{i=1}^C (\ln \gamma_{i,j,k}^{\text{exp}} - \ln \gamma_{i,j,k}^{\text{cal}})^2 \quad (13)$$

In Equation (13), γ are the activity coefficients, k is summed over the number of systems, i is summed over the number of the constituent, and j is summed over the total number of data points.

Usually, the interaction parameters of elements and chemical bonds were 100 K used in calculating the initial parameters. The optimization algorithm applied in the parameter estimation program is the quasi-Newton method.

The parameters for 43 group combinations are in Table A1 (the UNICAC parameter table). In most cases, the parameters were estimated as indicated above, without difficulty. However, less than adequate data are available, and for numerous group interactions, no or very little data could be found. At the same time, it was our goal to calculate the group interaction parameters for all possible binary combinations of groups, as shown in Table A1. At present, it is impossible to reach this goal entirely because of a serious lack of reliable experimental data. The UNICAC method needed 946 parameters but only had 535 parameters, missing 43.4% of the group-interaction parameters. Figure 1 presents the interaction parameters matrix of UNICAC.

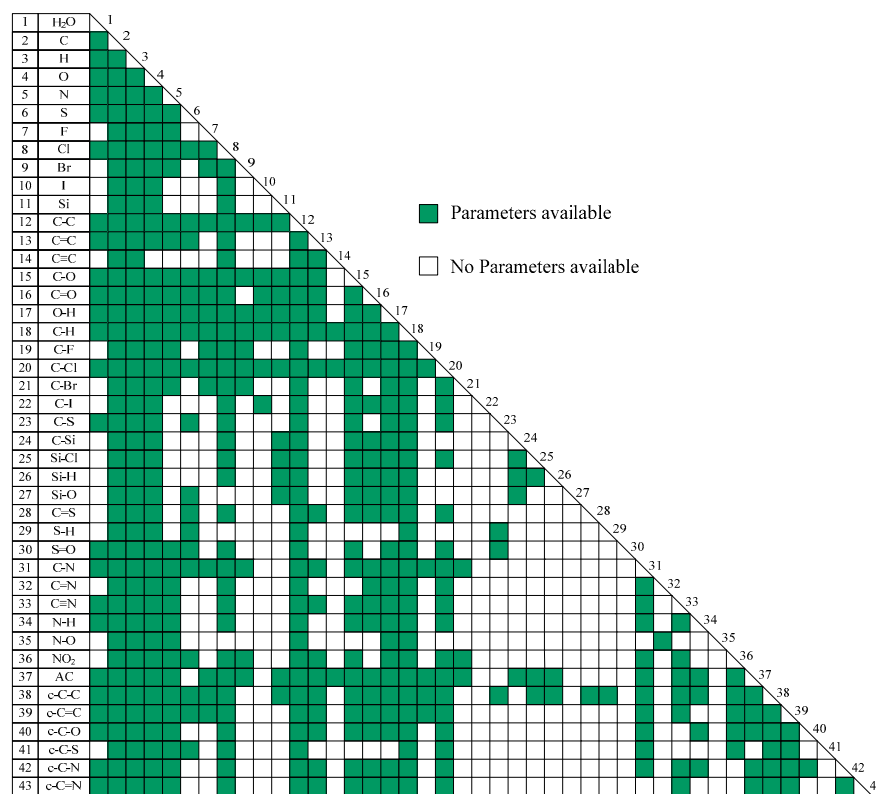


Figure 1. The interaction parameters matrix of elements and chemical bonds.

3. Results and Discussion

With the parameters in Table A1, it is now possible to predict the activity coefficients and vapor–liquid equilibria (VLEs) using the UNICAC model and Equation (14), for a large variety of binary and multicomponent systems.

$$py_i \hat{\phi}_i^V = x_i \gamma_i p_i^S \phi_i^S \exp \int_{p_i^S}^p \frac{V_i^L}{RT} dp \quad (14)$$

$$\sum y_i = 1; \sum x_i = 1$$

In Equation (14), for the binary VLE data, T is the temperature, P is the pressure, x_i is the liquid mole fraction of component i , and y_i is the vapor mole fraction of component i . $\hat{\phi}_i^V$ is the fugacity coefficient of component i , p_i^S is the saturated vapor pressure of the

component i , ϕ_i^S is the fugacity coefficient of the component i at p_i^S , V_i^L is the liquid molar volume at T , and the Poynting factor is 1.

Vapor–liquid phase equilibrium data are usually the vapor–liquid phase equilibrium data of the system measured via experimentation under isobaric or isothermal conditions, namely pressure, temperature, liquid phase composition, and vapor phase composition (T, P, x, y) , which can be divided into isobaric and isothermal vapor–liquid phase equilibrium data according to different measurement conditions.

For the isothermal vapor–liquid phase equilibrium data of the system measured experimentally under isothermal conditions, since the measurement temperature is unchanged, the calculation type of the vapor–liquid phase equilibrium is as follows: Given the temperature T and the liquid phase composition X , find the bubble point pressure P and vapor phase composition y , and the calculation expressions are shown in Equations (15) and (16).

$$p^{cal} = \sum_i \frac{x_i \gamma_i p_i^S}{y_i} \tag{15}$$

$$y_i^{cal} = \frac{x_i \gamma_i p_i^S}{y_i p^{cal}} \tag{16}$$

For the isobaric vapor–liquid phase equilibrium data of the system experimentally measured under isobaric conditions, the calculation type of the vapor–liquid phase equilibrium is as follows: given the pressure P and the liquid phase composition x , find the bubble point temperature T and the vapor phase composition y . Since, γ_i and p_i^S are functions of temperature, the results cannot be obtained directly, and so the method of trial and error is used to solve this. The calculation block diagram of bubble point temperature T and vapor phase composition y is shown in Figure 2.

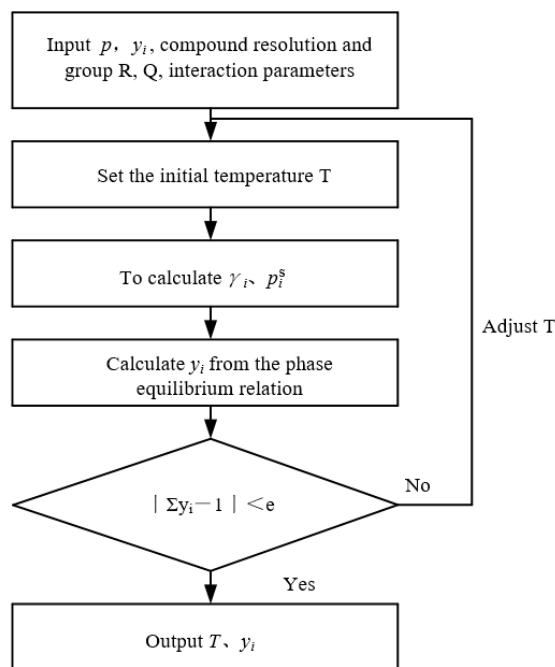


Figure 2. The diagram of calculation of bubble point temperature T and vapor composition y .

The temperature under the experimental conditions was taken as the initial temperature, and the convergence accuracy was set to 10^{-6} . Equations (17) and (18) are used for iterative calculation, and T is constantly adjusted to make the iterative calculation meet the convergence criteria.

$$T_{k+1} = T_k - \frac{f(T_k)}{f'(T_k)} \tag{17}$$

$$f(T) = \sum y_i - 1 \quad (18)$$

The ultimate test of the UNICAC method lies in its ability to predict activity coefficients for systems that were not included in the database, that is, the data set used to determine the parameters in Table A1. Therefore, we distinguish between the calculated results for systems contained in the database and predicted results for systems not contained in the database. The discussion of predictions is divided into three parts:

- Binary systems included in the database;
- Binary systems not included in the database;
- Ternary systems.

3.1. Binary Systems Included in the Database

The predicted and experimental vapor mole fraction, and the temperature or the pressure for binary VLEs included in the database used in the proposed method were compared.

The results of the UNIFAC method, UNIFAC (Dortmund), UNIFAC (Lyngby), ASOG method, and the new method are shown in Tables 2 and 3, respectively. The systems can be divided into different categories to illustrate the use of the new estimation method. *ARDP* stands for the relative deviation for pressure to experimental values, *ARDT* stands for the relative deviation for temperature to experimental values, and *ARDy* stands for the relative deviation for vapor-phase composition to experimental values.

Table 2. Comparison between predicted VLEs of experimental data for 1085 binary systems included in the database, and other group contribution methods.

Methods	N	ARDy	ARDP/ARDT
UNICAC	1085	5.18	2.69
UNIFAC	1050	5.26	4.18
UNIFAC (Dortmund)	1048	4.94	3.75
UNIFAC (Lyngby)	830	5.71	4.22
ASOG	1056	6.70	4.47

Table 3. Comparison of the predicted vapor mole fraction of experimental data for different categories included in the database.

System Family	N	UNICAC		UNIFAC		UNIFAC (Dortmund)		UNIFAC (Lyngby)		ASOG	
		ARDT/ARDT	ARDy	ARDT/ARDT	ARDy	ARDT/ARDT	ARDy	ARDT/ARDT	ARDy	ARDT/ARDT	ARDy
watery system	74	4.35	10.05	1.75	6.71	5.20	6.14	1.94	9.29	8.42	12.51
aromatic system	291	1.83	3.96	2.90	4.65	2.74	4.67	2.69	7.38	4.09	5.30
silicon containing system	12	2.82	2.39	1.66	0.68	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
sulfur system	18	1.04	1.93	5.48	3.26	5.08	2.22	n.a.	n.a.	1.37	2.57
acid system	78	3.22	8.98	13.94	16.33	11.77	14.43	23.47	11.38	10.79	28.68
ester containing system	126	2.61	4.99	3.31	4.82	2.85	4.20	3.85	3.82	2.92	5.36
aldehyde containing system	21	2.94	5.65	0.46	4.68	1.42	4.33	0.11	12.08	4.06	8.45
ketone containing system	144	2.38	4.79	1.63	3.25	1.44	4.03	4.95	3.30	1.91	3.53
fluorine containing system	27	2.62	4.05	2.57	6.20	0.46	8.53	n.a.	n.a.	4.68	6.28
chloride containing system	221	3.02	5.84	3.91	5.22	2.06	4.16	1.91	4.14	4.06	6.46
bromine containing system	9	2.31	1.65	13.21	2.72	3.13	1.87	n.a.	n.a.	22.30	2.92
iodine containing system	8	2.09	2.71	11.32	1.43	11.23	1.30	n.a.	n.a.	1.02	2.06
nitrogen containing system	119	4.42	4.70	7.44	6.47	4.96	5.04	3.04	5.43	10.98	15.27
alcohol containing system	399	2.07	4.19	2.86	4.62	3.06	4.74	2.64	4.65	2.77	4.42

n.a. (Not available): The compounds in the mixture cannot be described using the functional groups of the selected method.

The result shows a total of 1085 binary systems participating in the UNICAC model's bivariate interaction parameter regression. The vapor–liquid equilibria of some systems cannot be predicted by ASOG (2011), UNIFAC (2003), UNIFAC (Dortmund), and UNIFAC (Lyngby), due to the lack of group interaction parameters or compounds that cannot be resolved by the corresponding groups.

As can be seen from Table 3, UNIFAC (Dortmund), UNIFAC (Lyngby), and ASOG (2011) could not predict systems containing silicon compounds, such as dichlorosilane + trichlorosilane, etc. Only UNIFAC can predict a part of silica-containing organics, because it contains SiH_2 and SiO groups. Still, UNIFAC cannot resolve all silica-containing organics such as trichlorosilane and silicon tetrachloride.

In addition, UNIFAC (Lyngby) could not predict some systems containing fluorine and chloromethane, such as difluoromethane + propanol, difluoromethane + methanol, difluoromethane + ethanol, and other systems. Moreover, the model cannot predict the system containing sulfur, bromine, and iodine.

As seen in Tables 2 and 3, because of the small parameter matrices of modified UNIFAC (Lyngby), this model allows for calculations only for approximately 76% of those data that UNICAC can predict.

Furthermore, because many new groups have been introduced into the parameter matrix, UNICAC can predict the activity coefficients for systems that contain various mono- and dialkylated amides, carbonates, anhydrides, sulfones, epoxides, silicon, refrigerants, etc. Table 3 shows the improvement in the range of applicability for UNICAC. In all cases, the scope of UNICAC's applicability is larger than that of modified UNIFAC (Lyngby).

The UNICAC model has an ARDy of 5.18%, which is better than the ASOG model, and slightly worse than UNIFAC and its modified model. Meanwhile, the ARDP/ARDT for the UNICAC model is 2.69%, which is a better forecast. It is close to the predictive power of UNIFAC (Dortmund), and UNIFAC (Lyngby). When predicting the vapor–liquid phase equilibria of binary systems, the new model can predict both polar and non-polar systems, and is particularly suitable for predicting aromatic systems, silicon containing systems, sulfur systems, bromine containing systems, and iodine containing systems. However, the UNIFAC and UNIFAC (Dortmund) models have a much better prediction capability for the watery, aldehyde containing system, ketone containing system, ester containing system, and chloride containing system.

3.2. Binary Systems Not Included in the Database

In this section, the UNICAC model was assessed using binary mixtures not included in the database. One of the main advantages of the UNICAC method is its ability to predict activity coefficients for systems of this type from experimental information on normal systems, that is, those with only a few different functional groups. The results are shown in Table 4, and Table 5 illustrates this ability. Table 4 shows the calculated mean deviations in mole fraction, temperature, and pressure for various binary systems. The parameters (see Tables 1 and A1) allow for accurate predictions of systems containing alcohols such as methanol, ethanol, or 2-methyl-1-propanol. As shown in Table 5, the modified UNIFAC (Dortmund), modified UNIFAC (Lyngby), and ASOG cannot describe the system containing silicide; the usage of UNICAC leads to much better results. Table 6 shows the compounds that cannot be described in the binary systems not included in the database.

Because of the small parameter matrices of modified UNIFAC (Lyngby), Figures 3–6 are mainly limited to relatively simple compounds (alkanes, alkenes, alcohols, arenes, ketones, etc.) The complete VLE data sets (x , y , T , and P are given) can be described with all selected group contribution methods and which have passed consistency tests. Besides the predicted results using the five group contribution methods: UNICAC, UNIFAC modified UNIFAC (Dortmund), modified UNIFAC (Lyngby), and ASOG, a comparison of the predicted results from the five methods with the experimental values was made. Figure 3 for the ethanol + 2-methyl-1-propanol system indicates that the UNICAC method predicts vapor compositions well. The calculated and experimental vapor compositions are in good agreement for similar systems. Figure 4 shows good predictions for the systems toluene + 3-methyl-1-butanol; these favorable results suggest that the UNICAC method applies to systems containing toluene, and perhaps, other arenes. As Figure 5 shows, the results of the five methods for hexane+ 1-pentanol are the same. Figure 6 shows typical

examples of toluene and 4-methyl-2-pentanone. The UNICAC leads to much more reliable results than UNIFAC and ASOG.

Table 4. Deviations of predicted values from observed vapor–liquid equilibria for binary systems not included in the database using the UNICAC method.

System Component 1 + Component 2	System Number	P or T	n	Δy	ΔT or ΔP
ethanol + 2-methyl-1-propanol	1	101.33 kPa	14	0.0052	0.72 K
toluene + 3-methyl-1-butanol	2	101.33 kPa	15	0.0196	0.58 K
acetone + methanol	3	328.15 K	11	0.0132	1.36 kPa
1-hexene + 2-butanol	4	333.15 K	12	0.0160	3.59 kPa
hexane + 2-butanol	5	333.15 K	11	0.0130	2.25 kPa
hexane + 1-pentanol	6	323.15 K	13	0.0079	0.42 kPa
benzene + 2-methyl-1-propanol	7	101.33 kPa	31	0.0149	0.19 K
toluene + 1-pentanol	8	383.15 K	23	0.0126	1.92 kPa
toluene + 4-methyl-2-pentanone	9	323.15 K	26	0.0065	0.32 kPa
acetone + benzene	10	318.15 K	11	0.0091	0.72 kPa
methyl formate + dimethyl carbonate	11	101.33 kPa	14	0.0036	0.32 K
methanol + epoxy chloropropane	12	101.33 kPa	10	0.0103	0.87 K
trichlorosilane + silicon tetrachloride	13	98.70 kPa	11	0.0086	0.50 K
Diethyl disulfide + 2,2,4-trimethylpentane	14	368.15 K	8	0.0389	7.59 kPa
1,1-difluoroethane+ methanol	15	101.33 kPa	4	0.3815	25.16 K
water + propanoic acid	16	343.2 K	9	0.3090	23.98 kPa

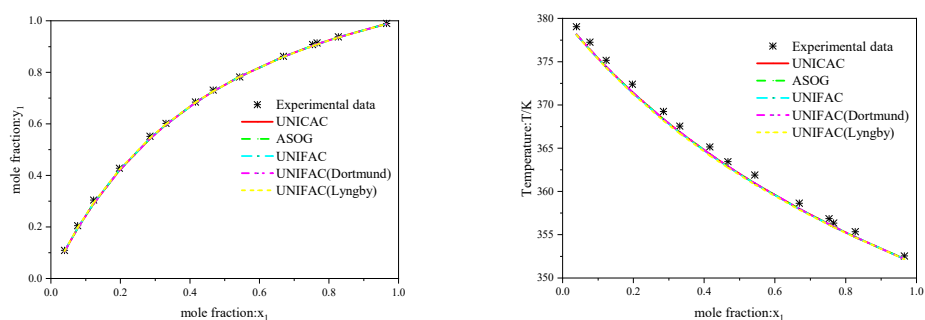
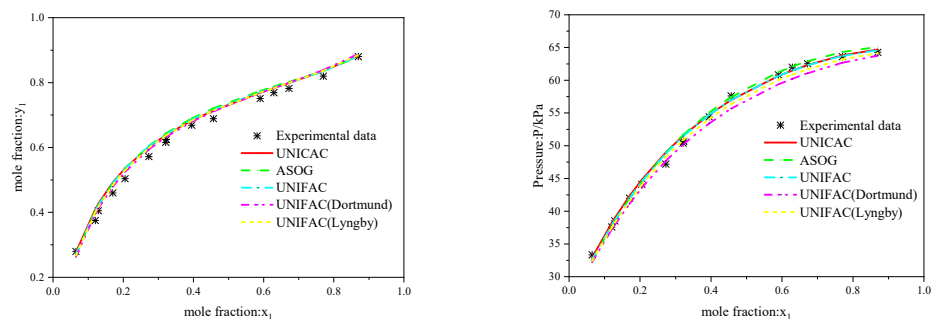
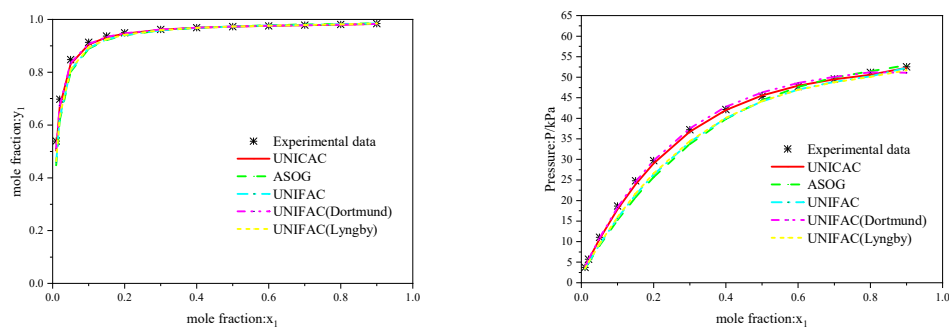
Table 5. Deviations of predicted values from observed vapor–liquid equilibria for binary systems not included in the database using different methods.

System Number	UNICAC		UNIFAC		UNIFAC (Dortmund)		UNIFAC (Lyngby)		ASOG	
	ARDy	ARDP/T	ARDy	ARDP/T	ARDy	ARDP/T	ARDy	ARDP/T	ARDy	ARDP/T
1	1.43	0.20	1.33	0.20	1.57	0.19	1.13	0.23	1.42	0.20
2	3.60	1.21	3.67	0.99	2.92	1.76	3.33	1.10	3.96	1.17
3	2.88	1.46	1.08	0.17	0.86	0.31	1.68	0.59	1.12	0.61
4	2.27	5.33	1.07	2.03	0.79	1.05	0.95	1.98	0.94	1.27
5	1.67	3.54	1.19	1.95	0.79	1.29	1.08	1.62	1.19	2.79
6	1.15	1.78	2.72	7.79	0.91	1.25	2.52	7.23	3.12	8.50
7	2.33	0.05	2.12	0.07	1.69	0.09	1.79	0.08	2.47	0.07
8	2.80	2.32	2.52	2.47	2.03	0.65	2.14	0.73	2.84	1.42
9	1.99	2.85	4.91	4.98	0.56	0.42	0.42	0.88	2.72	2.18
10	2.52	1.61	1.52	0.93	1.47	1.81	1.74	0.72	1.24	0.44
11	0.00	0.00	0.73	0.11	n.a.	n.a.	n.a.	n.a.	2.22	0.30
12	0.03	0.00	7.82	0.95	15.87	1.93	0.27	0.02	9.33	0.99
13	0.04	0.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
14	0.23	0.15	6.34	4.74	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
15	1.05	0.09	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	26.26	5.05
16	0.52	1.04	7.46	9.43	5.13	6.62	n.a.	n.a.	5.96	5.59
Average	1.53	1.35	3.18	2.63	2.88	1.45	1.55	1.38	4.63	2.18

Table 6. The compounds cannot be described in the binary systems not included in the database.

System Number	Component	UNICAC	ASOG	UNIFAC	UNIFAC (Dortmund)	UNIFAC (Lyngby)
11	methyl formate	✓	✓	✓	×	×
11	diethyl carbonate	✓	✓	✓	×	×
13	trichlorosilane	✓	×	×	×	×
13	silicon tetrachloride	✓	×	×	×	×
14	ethyl disulfide	✓	×	✓	×	×
15	1,1-difluoroethane	✓	✓	×	×	×
16	propanoic acid	✓	✓	✓	✓	×

✓: The compounds can be described using the functional groups of the selected method; ×: the compounds cannot be described.

**Figure 3.** Comparison of the predicted results from five methods with the experimental values of ethanol(1) + 2-methyl-1-propanol(2) at 1 atm.**Figure 4.** Comparison of the predicted results from five methods with the experimental values of toluene (1) + 3-methyl-1-butanol (2) at 1 atm.**Figure 5.** Comparison of the predicted results from five methods with the experimental values of hexane (1) + 1-pentanol (2) at 323.15 K.

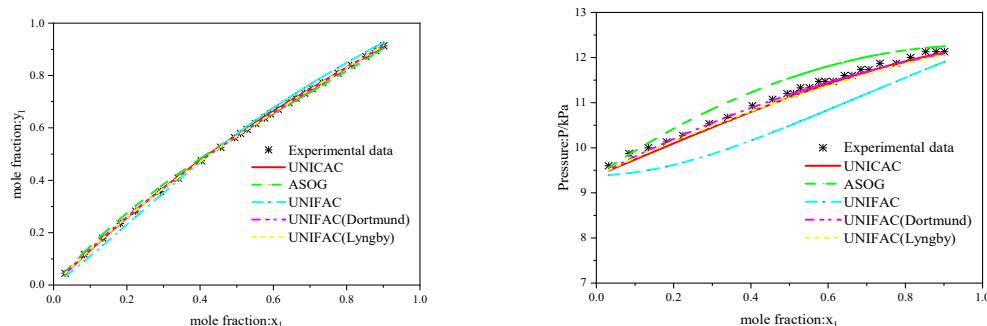


Figure 6. Comparison of the predicted results from five methods with the experimental values of toluene (1) + 4-methyl-2-pentanone (2) at 323.15 K.

3.3. Ternary Systems

The UNICAC method is directly applicable to multicomponent systems. Table 7 gives the vapor mole fraction, and the temperature or the pressure for binary VLEs calculated from the UNICAC method for ternary systems. No ternary systems were included in the database. There is an excellent agreement between the calculated and observed vapor–liquid equilibria for these systems.

Table 7. Deviations of predicted values from observed vapor–liquid equilibria for ternary systems using elements and chemical bonds contribution model.

System Component 1 + Component 2 + Component 3	P or T	n	Δy_1	Δy_2	ΔT or Δp
acetone + methanol + ethanol	101.33 kPa	83	0.0228	0.0123	1.09 K
methanol + ethanol + 1-propanol	101.33 kPa	45	0.0224	0.0122	0.75 K
acetone + methanol + 2-propanol	328.15 K	27	0.0206	0.0163	2.02 kPa
2,3-dimethyl-butane + methanol + acetone	101.33 kPa	27	0.0247	0.0236	2.36 K
methanol + 2-methylbutane+ isoprene	101.33 kPa	13	0.0489	0.0534	0.69 K
methanol + heptane + toluene	101.33 kPa	8	0.0065	0.0049	0.21 K
acetone + ethanol + hexane	328.15 K	21	0.0271	0.0141	12.20 kPa
hexane + ethanol + benzene	328.15 K	43	0.0206	0.0253	4.81 kPa
ethanol + benzene + heptane	53.33 kPa	50	0.0232	0.0176	1.08 K
ethanol + benzene + heptane	101.33 kPa	47	0.0264	0.0199	0.99 K
benzene + heptane + 1-propanol	348.15 K	77	0.0273	0.0153	1.83 kPa
acetone + 2-methyl-butane + isoprene	101.33 kPa	15	0.0251	0.0205	2.22 K
2-butanone + 3-pentanone + 4-methyl-2-pentanone	101.33 kPa	64	0.0214	0.0085	0.54 K

4. Conclusions

A generalized model for the prediction of the activity coefficients of nonelectrolytes is proposed. Phase equilibrium data were used to generate many elements/chemical bonds-interaction parameters. These are useful for predicting activity coefficients in binary and multicomponent systems where little or no experimental information exists. The method gives good predictions for a large variety of systems, and should therefore provide a valuable tool for solving practical phase equilibrium problems as encountered in the chemical process design.

Author Contributions: H.L. and X.L.: Formal analysis, Validation, Visualization, Writing—original draft; X.S.: Resources, Supervision, Validation, Project administration; Y.W. and W.Z.: Formal analysis, Investigation; L.X. and S.X.: Conceptualization, Methodology, Software, Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (No. 22178190, 22008129).

Data Availability Statement: The data presented in this study are available from the corresponding author upon request.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

n	The number of data sets for VLEs
N	The number of systems can be predicted using the functional groups of the selected method
P	Pressure
q	Pure component area parameter
Q	Group area parameter
r	Pure component volume parameter
R	Gas constant (without subscript)
R_k	Group volume parameter (with subscript)
T	Temperature
a_{kl}	UNICAC binary interaction parameter
x	Liquid-phase mole fraction
X	Liquid-phase group fraction
y	Vapor-phase mole fraction
z	Lattice coordination number, a constant here set, equal to ten
γ_i	Activity coefficient of component i
Γ_k	The group residual activity coefficient
$\Gamma_k^{(i)}$	The residual activity coefficient of group k in a reference solution containing only molecules of type i
x_i	The mole fraction of component i
θ_i	The area fraction
ϕ_i	The segment fraction
C	Combinatorial
R	Residual
i, j, k	Components i, j, and k
ΔP	The mean absolute deviation for pressure to experimental values
ΔT	The mean absolute deviation for temperature to experimental values
Δy	The mean absolute deviation for vapor-phase composition to experimental values
ARDP	The mean relative deviation for pressure to experimental values
ARDT	The mean relative deviation for temperature to experimental values
ARDy	The mean relative deviation for vapor-phase composition to experimental values

Appendix A

Table A1. The interaction parameters of elements and chemical bonds/K.

j \ k		H ₂ O	C	H	O	N	S	F	Cl	Br
		H ₂ O	0.000	3050.144	2828.223	1216.658	1389.824	−257.189	100.000	1206.203
C	−49.102	0.000	1700.283	571.297	205.332	757.536	138.321	−201.219	536.176	
H	−3.718	2873.440	0.000	98.958	123.882	342.010	39.479	461.176	407.430	
O	−1062.727	−305.461	1599.359	0.000	889.030	−628.877	457.628	−37.052	−462.539	
N	−1058.869	312.450	1277.751	1471.891	0.000	20.124	−349.945	−169.885	−85.786	
S	846.310	229.472	780.556	537.378	−143.997	0.000	100.000	−25.555	100.000	
F	100.000	596.773	618.385	−146.405	65.505	100.000	0.000	389.055	−44.514	
Cl	−464.586	101.578	274.945	211.270	1158.592	102.975	724.708	0.000	−37.348	
Br	100.000	287.079	237.387	245.886	67.844	100.000	−468.308	−121.071	0.000	
I	100.000	441.250	211.749	661.227	100.000	100.000	100.000	−170.467	100.000	
Si	100.000	265.550	−33.247	292.652	100.000	100.000	100.000	321.030	100.000	
C-C	−208.889	613.609	2327.050	1819.310	442.833	58.474	−170.543	135.599	518.587	
C=C	106.845	2039.925	309.397	0.801	581.564	−0.672	100.000	24.489	100.000	
C≡C	100.000	−253.836	919.003	100.000	100.000	100.000	100.000	520.177	100.000	
C-O	21.533	544.100	2901.417	2596.894	657.528	638.406	374.031	707.922	853.301	

Table A1. Cont.

j \ k		H ₂ O	C	H	O	N	S	F	Cl	Br
C=O		180.846	1656.696	1414.548	2663.021	355.356	597.766	413.476	413.183	100.000
O-H		-54.190	1668.997	2049.469	856.008	2044.495	468.492	1437.554	1256.615	2696.125
C-H		-460.178	-830.150	1785.944	-853.732	814.801	-436.887	119.278	602.441	-615.367
C-F		100.000	-774.669	1369.966	-967.107	143.604	100.000	902.691	-30.472	-400.790
C-CL		-541.494	747.975	1172.662	732.129	-26.174	708.055	424.076	-481.656	-188.007
C-Br		100.000	261.758	376.489	170.260	47.283	100.000	-184.911	275.332	-59.922
C-I		100.000	440.046	203.820	659.385	100.000	100.000	100.000	-102.982	100.000
C-S		-818.786	474.728	1132.954	340.821	100.000	-793.953	100.000	-316.956	100.000
C-Si		100.000	342.567	34.080	393.668	100.000	100.000	100.000	-47.721	100.000
Si-Cl		100.000	-439.997	313.197	225.691	100.000	100.000	100.000	334.908	100.000
Si-H		100.000	153.966	565.312	192.945	100.000	100.000	100.000	-70.471	100.000
Si-O		100.000	66.977	105.676	110.041	100.000	100.000	100.000	100.000	100.000
C=S		100.000	-379.835	559.488	-135.257	100.000	799.209	100.000	-144.947	100.000
S-H		100.000	156.071	102.836	100.000	100.000	37.410	100.000	100.000	100.000
S=O		726.193	159.024	221.009	74.627	100.000	-28.386	100.000	-221.204	100.000
C-N		-1952.965	-1652.983	1530.693	-1625.916	820.715	93.345	358.580	413.852	32.076
C=N		100.000	431.147	-56.654	283.796	283.797	100.000	100.000	270.226	100.000
C≡N		134.236	1241.637	1907.937	283.835	-178.635	100.000	100.000	25.700	100.000
N-H		2305.362	552.196	1130.348	1308.921	1356.805	100.000	100.000	1902.413	100.000
N-O		100.000	295.673	477.315	-147.975	-147.974	100.000	100.000	100.000	100.000
NO2		100.000	749.446	511.939	-97.284	-363.979	144.011	100.000	5.617	-259.222
benzene ring		-1449.963	1199.247	321.987	518.333	456.047	100.000	-504.803	-20.526	132.280
c-C-C		-371.653	303.435	166.746	1440.309	359.953	540.339	111.453	1701.947	100.000
c-C=C		-950.320	596.565	781.186	-525.182	403.778	-145.468	192.259	-20.109	100.000
c-C-O		-1041.847	1463.739	1616.941	-1002.002	313.169	100.000	100.000	-820.396	100.000
c-C-S		100.000	138.671	383.112	-41.619	27.643	-12.862	100.000	230.860	100.000
c-C-N		-906.042	1685.589	1555.754	1026.512	-532.090	100.000	100.000	-9.057	100.000
c-C=N		69.075	353.717	420.888	507.191	162.534	100.000	100.000	101.612	100.000
j \ k		H ₂ O	C	H	O	N	S	F	Cl	Br
H ₂ O		100.000	100.000	968.856	1302.196	100.000	2351.668	270.868	221.262	2742.986
C		18.127	127.745	209.497	-150.495	-16.663	119.445	1516.056	304.543	2404.675
H		421.015	278.618	2328.983	240.528	244.831	-126.927	-93.161	73.297	2673.215
O		-742.230	542.032	895.263	-433.118	100.000	-810.412	-1118.597	-891.500	-219.268
N		100.000	100.000	1619.787	931.205	100.000	1696.658	368.314	135.428	-98.845
S		100.000	100.000	7.527	305.250	100.000	-282.557	620.096	526.984	610.282
F		100.000	100.000	-98.852	100.000	100.000	-289.695	283.065	-274.047	533.812
Cl		-361.900	-283.849	-257.975	265.478	630.377	-366.450	50.348	-335.161	660.563
Br		100.000	100.000	438.239	100.000	100.000	350.883	100.000	202.701	-690.481
I		0.000	100.000	435.601	100.000	100.000	299.981	566.429	509.232	-316.375
Si		100.000	0.000	177.628	100.000	100.000	171.594	233.123	171.593	-188.973
C-C		596.769	231.042	0.000	-73.579	-126.760	404.205	1591.987	1516.314	-22.436
C=C		100.000	100.000	1426.824	0.000	14.965	56.577	-73.713	-12.606	1688.310
C≡C		100.000	100.000	474.952	514.193	0.000	100.000	100.000	100.000	919.003
C-O		-56.474	161.983	-68.851	600.696	100.000	0.000	1035.930	2641.120	2520.279
C=O		99.877	1001.694	2609.060	332.559	100.000	985.583	0.000	2401.832	862.502
O-H		907.583	831.332	1610.931	1338.807	100.000	878.186	-95.513	0.000	1972.909
C-H		-980.332	-270.054	-774.930	-729.573	366.223	1240.032	-693.036	-941.209	0.000
C-F		100.000	100.000	-608.179	100.000	100.000	99.559	55.450	-958.187	1358.684
C-CL		-526.103	125.445	529.495	-244.739	698.727	-313.712	167.680	116.231	-88.721
C-Br		100.000	100.000	763.867	100.000	100.000	188.669	100.000	12.756	450.176
C-I		-955.091	100.000	433.768	100.000	100.000	297.532	564.483	508.589	-358.160
C-S		100.000	100.000	-40.450	100.000	100.000	257.259	100.000	257.259	1112.183
C-Si		100.000	-25.401	164.683	100.000	100.000	311.277	206.104	311.278	-238.823
Si-Cl		100.000	-21.198	-6.673	100.000	100.000	79.200	242.662	79.200	210.578
Si-H		100.000	-202.672	-104.099	100.000	100.000	76.197	212.738	76.197	676.158
Si-O		100.000	122.537	-8.462	100.000	100.000	99.003	99.004	99.004	111.281

Table A1. Cont.

j \ k		H ₂ O	C	H	O	N	S	F	Cl	Br
	c-C-O	100.000	−819.599	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	c-C-S	100.000	230.860	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	c-C-N	100.000	−9.061	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	c-C=N	100.000	101.611	100.000	100.000	100.000	100.000	100.000	100.000	100.000
j \ k		H ₂ O	C	H	O	N	S	F	Cl	Br
	H ₂ O	100.000	100.000	−257.188	990.677	100.000	382.555	184.834	100.000	100.000
	C	94.306	161.761	45.536	111.353	572.409	648.163	40.330	638.395	−17.545
	H	−64.946	46.822	−241.549	−31.576	−345.132	−450.802	119.516	828.881	712.230
	O	−241.929	100.000	25.715	1324.313	205.694	−880.684	880.701	−355.803	−973.086
	N	100.000	100.000	100.000	−914.472	291.981	−956.003	1328.214	−496.665	−137.784
	S	−351.720	−94.221	33.313	−143.998	100.000	100.000	100.000	100.000	−143.997
	F	100.000	100.000	100.000	53.785	100.000	100.000	100.000	100.000	100.000
	Cl	99.021	100.000	62.633	−381.884	−442.091	721.657	−373.448	100.000	−29.934
	Br	100.000	100.000	100.000	67.924	100.000	100.000	100.000	100.000	67.807
	I	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	Si	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	C-C	−434.381	69.707	335.332	1790.894	−205.603	294.991	41.932	440.890	−624.975
	C=C	−0.439	100.000	100.000	364.448	100.000	−55.299	100.000	100.000	−317.034
	C≡C	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	C-O	568.968	100.000	456.565	235.841	100.000	−261.918	323.491	100.000	−73.121
	C=O	597.765	100.000	100.000	−94.205	522.127	−110.526	274.243	100.000	100.000
	O-H	476.542	100.000	4.210	922.708	996.941	49.129	1094.051	996.941	1169.604
	C-H	−165.808	114.915	−122.184	1398.731	226.569	652.083	116.868	393.119	−704.437
	C-F	100.000	100.000	100.000	239.166	100.000	100.000	100.000	100.000	100.000
	C-Cl	−302.206	100.000	931.013	660.485	−283.517	267.171	−190.958	100.000	−301.834
	C-Br	100.000	100.000	100.000	47.282	100.000	100.000	100.000	100.000	47.309
	C-I	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	C-S	100.000	186.230	−6.368	100.000	100.000	100.000	100.000	100.000	100.000
	C-Si	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	Si-Cl	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	Si-H	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	Si-O	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	C=S	0.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	S-H	100.000	0.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
	S=O	100.000	100.000	0.000	100.000	100.000	100.000	100.000	100.000	100.000
	C-N	100.000	100.000	100.000	0.000	277.156	523.501	−1012.995	100.000	−799.139
	C=N	100.000	100.000	100.000	455.538	0.000	100.000	100.000	−760.569	100.000
	C≡N	100.000	100.000	100.000	1278.710	100.000	0.000	1543.830	100.000	218.230
	N-H	100.000	100.000	100.000	146.828	100.000	376.480	0.000	100.000	100.000
	N-O	100.000	100.000	100.000	100.000	−147.973	100.000	100.000	0.000	100.000
	NO ₂	100.000	100.000	100.000	−431.148	100.000	109.741	100.000	100.000	0.000
	benzene ring	100.000	100.000	100.000	−130.231	100.000	490.002	−836.341	100.000	214.480
	c-C-C	−212.056	281.620	100.000	591.386	100.000	474.862	−165.708	100.000	382.157
	c-C=C	100.000	100.000	100.000	149.690	100.000	332.719	100.000	100.000	149.689
	c-C-O	100.000	100.000	100.000	−842.900	100.000	100.000	−814.137	100.000	487.471
	c-C-S	100.000	100.000	100.000	27.668	100.000	100.000	100.000	100.000	27.668
	c-C-N	100.000	100.000	100.000	534.156	100.000	202.015	94.093	100.000	100.000
	c-C=N	100.000	100.000	100.000	100.000	100.000	317.165	100.000	100.000	100.000
j \ k		H ₂ O	C	H	O	N	S	F	Cl	Br
	H ₂ O	2428.601	873.972	595.148	892.328	100.000	882.580	1299.519		
	C	2342.979	−18.356	−194.010	−19.844	541.556	−224.601	−350.159		
	H	−137.045	878.648	−95.298	−210.397	419.870	898.204	278.609		
	O	−1125.752	−364.521	−1018.988	−938.065	−196.273	432.264	190.541		
	N	25.391	−295.645	−999.407	518.323	−75.219	−557.928	−68.028		

Table A1. Cont.

j \ k	H ₂ O	C	H	O	N	S	F	Cl	Br
S	100.000	−303.958	11.924	100.000	11.693	100.000	100.000		
F	−710.003	−339.403	208.905	100.000	100.000	100.000	100.000		
Cl	−493.659	−21.130	−327.417	167.558	232.735	−199.888	−199.938		
Br	93.599	100.000	100.000	100.000	100.000	100.000	100.000		
I	100.000	100.000	100.000	100.000	100.000	100.000	100.000		
Si	151.251	−363.068	100.000	100.000	100.000	100.000	100.000		
C-C	−199.914	340.715	219.161	139.458	−53.684	405.048	−265.779		
C=C	640.175	88.567	−171.285	−111.968	100.000	917.352	917.352		
C≡C	184.563	100.000	100.000	100.000	100.000	100.000	100.000		
C-O	−259.606	90.208	280.205	270.645	100.000	591.009	591.005		
C=O	−101.292	1257.209	−106.909	930.691	100.000	−182.817	171.861		
O-H	610.997	2118.223	2240.058	614.914	100.000	2023.057	2023.057		
C-H	−616.763	−767.783	814.025	835.370	186.503	212.721	−174.054		
C-F	135.777	−619.326	177.583	100.000	100.000	100.000	100.000		
C-Cl	−391.580	1024.101	−427.959	386.027	133.660	887.304	887.304		
C-Br	52.191	100.000	100.000	100.000	100.000	100.000	100.000		
C-I	100.000	100.000	100.000	100.000	100.000	100.000	100.000		
C-S	100.000	10.317	100.000	100.000	100.000	100.000	100.000		
C-Si	220.297	100.000	100.000	100.000	100.000	100.000	100.000		
Si-Cl	−120.496	465.756	100.000	100.000	100.000	100.000	100.000		
Si-H	−234.096	670.426	100.000	100.000	100.000	100.000	100.000		
Si-O	100.000	100.000	100.000	100.000	100.000	100.000	100.000		
C=S	100.000	88.545	100.000	100.000	100.000	100.000	100.000		
S-H	100.000	253.140	100.000	100.000	100.000	100.000	100.000		
S=O	100.000	100.000	100.000	100.000	100.000	100.000	100.000		
C-N	−1837.934	−1291.486	86.820	205.080	86.820	42.246	100.000		
C=N	100.000	100.000	100.000	100.000	100.000	100.000	100.000		
C≡N	−284.559	685.778	685.778	100.000	100.000	479.422	479.422		
N-H	−51.561	1263.565	100.000	466.869	100.000	226.896	100.000		
N-O	100.000	100.000	100.000	100.000	100.000	100.000	100.000		
NO ₂	179.307	561.474	194.215	731.096	194.215	100.000	100.000		
benzene ring	0.000	625.329	583.208	642.880	100.000	71.630	−19.934		
c-C-C	410.757	0.000	529.782	−197.735	184.022	916.388	293.016		
c-C=C	−1071.029	−907.829	0.000	−1074.457	−702.276	123.804	123.695		
c-C-O	−1012.367	283.298	−265.763	0.000	100.000	248.190	100.000		
c-C-S	100.000	510.702	−92.852	100.000	0.000	100.000	100.000		
c-C-N	750.502	−355.021	−364.322	−593.329	100.000	0.000	−292.099		
c-C=N	−350.334	685.453	−540.339	100.000	100.000	−125.066	0.000		

References

- Shang, Q.; Xiao, J.; Liu, X.; Ling, Y.; Liu, W.; Cui, G.; Shi, X.; Xia, S.; Tang, B. Isobaric vapor-liquid equilibrium and distillation process design for separating ketones in biomass pyrolysis oil. *J. Chem. Thermodyn.* **2022**, *164*, 106622. [\[CrossRef\]](#)
- Domańska, U. Experimental data of fluid phase equilibria-correlation and prediction models: A review. *Processes* **2019**, *7*, 277. [\[CrossRef\]](#)
- Lee, H.Y.; Yeh, M.H.; Chen, Y.Y.; Chen, C.L. Design and control of a comprehensive ethylenediamine (EDA) process with external/internal heat integration. *Sep. Purif. Technol.* **2022**, *293*, 121137. [\[CrossRef\]](#)
- Kontogeorgis, G.M.; Folas, G.K. *Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories*; Wiley: New York, NY, USA, 2010.
- Prausnitz, J.M.; Lichtenthaler, R.N.; Azevedo, E.G. *Molecular Thermodynamics of Fluid-Equilibria*, 3rd ed.; Pearson Education: Upper Saddle River, NJ, USA, 1999.
- Lohmann, J.; Joh, R.; Gmehling, J. From UNIFAC to modified UNIFAC (Dortmund). *Ind. Eng. Chem. Res.* **2001**, *40*, 957–964. [\[CrossRef\]](#)
- Tochigi, K.; Tiegs, D.; Gmehling, J. Determination of new ASOG parameters. *J. Chem. Eng. Jpn.* **1990**, *23*, 453–463. [\[CrossRef\]](#)
- Tochigi, K.; Gmehling, J. Determination of new ASOG parameters-extension and revision. *J. Chem. Eng. Jpn.* **2011**, *44*, 304–306. [\[CrossRef\]](#)

9. Robles, P.A.; Morales, J.W.; Cisternas, L.A. Modeling of liquid-liquid equilibrium for binary and ternary systems containing ionic liquids with the hexafluorophosphate anion using the ASOG method. *Fluid Phase Equilib.* **2016**, *429*, 119–126. [[CrossRef](#)]
10. Fredenslund, A.; Jones, R.L.; Prausnitz, J.M. Group-contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J.* **1975**, *21*, 1086–1099. [[CrossRef](#)]
11. Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method*; Elsevier: Amsterdam, The Netherlands, 1977.
12. Jørgensen, S.S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. Vapor-liquid equilibria by UNIFAC group contribution. revision and extension. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18*, 714–722. [[CrossRef](#)]
13. Gmehling, J.; Rasmussen, P.; Fredenslund, A. Vapor-liquid equilibria by UNIFAC group contribution. revision and extension 2. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118–127. [[CrossRef](#)]
14. Macedo, E.A.; Weidlich, U.; Gmehling, J.; Rasmussen, P. Vapor-liquid equilibria by UNIFAC group contribution. revision and extension 3. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 676–678. [[CrossRef](#)]
15. Tiegs, D.; Gmehling, J.; Rasmussen, P.; Fredenslund, A. Vapor-liquid equilibria by UNIFAC group contribution. Revision and extension 4. *Ind. Eng. Chem. Res.* **1987**, *26*, 159–161. [[CrossRef](#)]
16. Hansen, H.K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. Vapor-liquid equilibria by UNIFAC group contribution. revision and extension 5. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352–2355. [[CrossRef](#)]
17. Wittig, R.; Lohmann, J.; Gmehling, J. Vapor-liquid equilibria by UNIFAC group contribution. 6 revision and extension. *Ind. Eng. Chem. Res.* **2003**, *42*, 183–188. [[CrossRef](#)]
18. Larsen, B.L.; Rasmussen, P.; Fredenslund, A. A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274–2286. [[CrossRef](#)]
19. Gmehling, J.; Li, J.; Schiller, M. A modified UNIFAC model. 2. present parameter matrix and results for different thermodynamic properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178–193. [[CrossRef](#)]
20. Gmehling, J.; Lohmann, J.; Jakob, A.; Li, J.; Joh, R. A modified UNIFAC (Dortmund) model. 3. revision and extension. *Ind. Eng. Chem. Res.* **1998**, *37*, 4876–4882. [[CrossRef](#)]
21. Gmehling, J.; Wittig, R.; Lohmann, J. A modified UNIFAC (Dortmund) model. 4. revision and extension. *Ind. Eng. Chem. Res.* **2002**, *44*, 1678–1688. [[CrossRef](#)]
22. Jakob, A.; Grensemann, H.; Lohmann, J.; Gmehling, J. Further development of modified UNIFAC (Dortmund): Revision and extension 5. *Ind. Eng. Chem. Res.* **2006**, *45*, 7924–7933. [[CrossRef](#)]
23. Constantinescu, D.; Gmehling, J. Further development of modified UNIFAC (Dortmund): Revision and extension 6. *J. Chem. Eng. Data.* **2016**, *61*, 2738–2748. [[CrossRef](#)]
24. González, H.E.; Abildskov, J.; Gani, R. A method for prediction of UNIFAC group interaction parameters. *AIChE J.* **2007**, *53*, 1620–1632. [[CrossRef](#)]
25. Klauck, M.; Richter, S.; Hähnel, T.; Schmelzer, J.; Kalies, G. Modified UNIFAC (Dortmund) parameters for the interaction between the amino group at cycloaliphatic hydrocarbon and the hydroxyl group. *Ind. Eng. Chem. Res.* **2019**, *58*, 21730–21738. [[CrossRef](#)]
26. Qin, Y.B.; Zhang, H.; Liu, B.L.; Li, N.X. Experimental measurements and thermodynamic modeling of VLE for strong-zeotropic ternary system of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf)+ ethane (R170)+ tetrafluoromethane (R14). *Ind. Eng. Chem. Res.* **2019**, *58*, 2333–2342. [[CrossRef](#)]
27. Nayak, P.R.; Akhouri, B.P. Vapor-liquid equilibrium in methanol+ water system and modeling from 298.15 to 373.15 K. *Mater. Today Proc.* **2022**, *59*, 506–509. [[CrossRef](#)]
28. Li, J.; Xia, L.; Xiang, S.G. A new method based on elements and chemical bonds for organic compounds critical properties estimation. *Fluid Phase Equilib.* **2016**, *417*, 1–6. [[CrossRef](#)]
29. Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection*; 34 parts DECHEMA chemistry data series; DECHEMA: Frankfurt, Germany, 1977; Volume I.
30. Bondi, A. van der Waals volumes and radii. *J. Phys. Chem.* **1964**, *68*, 441–451. [[CrossRef](#)]