

Estimation of the enthalpy of vaporization at normal boiling temperature of organic compounds by a new group contribution method

Soheil Abdi, Kamyar Movagharnejad*, Habib Ghasemitabar

Babol Noshiravani University of Technology, Faculty of Chemical Engineering, Babol, Iran

ARTICLE INFO

Article history:

Received 15 March 2018

Received in revised form

13 June 2018

Accepted 14 June 2018

Available online 22 June 2018

Keywords:

Enthalpy of vaporization

Normal boiling temperature

Group contribution method

Organic compounds

ABSTRACT

We need to know the thermo-physical properties of different compounds in order to design, model or optimize the industrial processes. Among various thermo-physical properties, enthalpy of vaporization at normal boiling temperature is one of the most important and useful properties in industrial processes. Although experimental data are available from various sources, but in order to complete these data, theoretical methods may be required to estimate and predict this property. The new group contribution method which can be regarded as a modification to the original Joback and Reid method gives more accurate estimations of the enthalpy of vaporization at normal boiling temperature of organic compounds. Group contribution values have been optimized using 3950 experimental data of organic components with a molecular weight range of 28–565 (g mol^{-1}) and number of carbon atoms range of 1–40. Checking the results of the new method on 3950 different organic compounds shows an average absolute error of 0.620 kJ/mol and the percentage average relative error of 1.683%. The results of the new method have been compared with the original method of Joback and Reid, and the Kolska, Ruzicka and Gani method. The results showed the better agreement between the predictions of the present method and the experimental data, comparing to the other group contribution methods.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

A good knowledge about the thermo-physical properties is essential for every engineering design and calculation. For Example, an engineer would not be able to design a bridge without having detailed information about the properties of concrete or steel. Similarly, a good knowledge of thermodynamic properties are required for any chemical engineer in order to design a variety of products, processes or industrial equipment [1]. Experimental methods and laboratory measurements of thermo-physical properties require a lot of time and money in many cases, but using appropriate computing techniques, these measurements can be avoided in many cases [2]. Although experimental and laboratory methods are more accurate and reliable, but all of these methods require the proper laboratory equipment and sufficient amount of the compounds of high purity which are not always available. At the other hand, some testing compounds may decompose during

the measuring test which is a serious problem. In addition, the use of hazardous compounds restricts the application of these experimental methods. Therefore, some non-experimental theoretical methods can be used to substitute the testing procedure [3]. Although the predicted properties are not as accurate as the experimental data, but for the engineering most applications, the accuracy of these theoretical estimations seems sufficient. Estimation methods can also be used to check the results of the laboratory routine works.

Among the thermo-physical properties, the enthalpy of vaporization at normal boiling temperature is one of the most important properties of the vapor-liquid equilibrium processes. The enthalpy of vaporization at normal boiling temperature is the difference between the enthalpy of saturated vapor and the enthalpy of the saturated liquid at the normal boiling temperature [4]. This property is widely used in the design of processes involving vapor-liquid equilibrium, such as distillation towers, evaporators and dryers working at atmospheric pressure. The enthalpy of vaporization at normal boiling temperature can also be used to estimate some other thermodynamic properties, such as solubility parameters. In addition, this property can be used to predict the vapor pressure of

* Corresponding author.

E-mail addresses: movagharnejad@yahoo.com, k-movaghar@nit.ac.ir (K. Movagharnejad).

pure compounds [3].

In general, various methods have been proposed to estimate the enthalpy of vaporization at normal boiling temperature. For Example, the first generation of equations used to predict the enthalpy of vaporization were based on the following vapor pressure relationships.

$$\psi = \frac{\Delta H_v}{RT_c \Delta Z_v} = \frac{-d \ln P_{vpr}}{d(1/T_r)} \quad (1)$$

In relation (1), ΔH_v is the enthalpy of vaporization, R is the universal gas constant, T_c is the critical temperature, ΔZ_v is the change of the compressibility coefficient, P_{vpr} is the reduced vapor pressure and T_r is the reduced temperature. According to Equation (1), the function ψ and so the ΔH_v can be derived from the vapor pressure equation. In these relationships, at least one other physical property, such as critical temperature, is required to estimate the enthalpy of vaporization at normal boiling temperature. For Example, Riedel [5] presented the equation (2) for estimating of the enthalpy of vaporization at normal boiling temperature:

$$\Delta H_{vb} = 1.093 RT_c T_{br} \frac{\ln P_c - 1.013}{0.930 - T_{br}} \quad (2)$$

In relation (2), T_{br} is the reduced normal boiling temperature and P_c is the critical pressure. Chen [6] presented the equation (3) for estimating of the enthalpy of vaporization at normal boiling temperature:

$$\Delta H_{vb} = RT_c T_{br} \frac{3.978 T_{br} - 3.958 + 1.555 \ln P_c}{1.07 - T_{br}} \quad (3)$$

Also, Vetere [7] presented the equation (4) for estimating of the enthalpy of vaporization at normal boiling temperature:

$$\Delta H_{vb} = RT_b \frac{0.89584 T_{br} - 0.69431 + 0.4343 \ln P_c}{0.37961 - 0.37306 T_{br}} + 0.15075 P_c^{-1} T_{br}^{-2} \quad (4)$$

The accuracy of these relationships depends on the accuracy and validity of the physical properties used in those correlations. In addition, if the physical properties are not available, the estimation of the enthalpy of vaporization at normal boiling temperature would not be possible by this class of relationships. Cachadina and Mulero [8] examined ten different empirical correlations of this kind and concluded that all of them have a good total relative error, but none of them were well suited for all kinds of organic compounds and groups. This final conclusion suggests that these empirical models are not comprehensive for all compounds and more complicated models are needed for estimation of this property [9].

On the other hand, group contribution methods are also used to estimate the enthalpy of vaporization at normal boiling temperature. In these methods only group contribution values and chemical structure of compounds are needed and their calculations are simple and inexpensive [10]. Group contribution methods are used to predict the different thermo-physical properties of pure components and mixtures. For Example Joback and Reid [11], Constantinou and Gani [12], Marrero and Gani [13] presented group contribution methods for estimation of critical properties. Also Di Nicola et al. [14] presented group contribution methods for the estimation of second virial coefficients. Also Gardas and Coutinho [15] presented a group contribution method for the estimation of heat capacity of ionic liquids.

Joback and Reid presented the equation (5) for the estimation of enthalpy of vaporization at normal boiling temperature:

$$\Delta H_{vb} = 15.30 + \sum_i n_i (\Delta H_{vb})_i \quad (5)$$

In this relation, ΔH_{vb} is the enthalpy of vaporization at normal boiling temperature, n_i is the number of the group contribution of type i , $(\Delta H_{vb})_i$ is the group contribution of type i . In Table 1, the values of group contribution values $(\Delta H_{vb})_i$ are given by the Joback and Reid method.

Joback and Reid examined 368 organic compounds and according to equation (5). They calculated the enthalpy of vaporization at normal boiling temperature of these compounds, the average relative error was 3.9% and the absolute average error was 1.27 kJ/mol.

Also, Kolska, Ruzicka and Gani presented the equation (6) for the estimation of the enthalpy of vaporization at normal boiling temperature [10]:

$$\Delta H_{vb} = h_b + \sum_i N_i C_i + w \sum_j M_j D_j + z \sum_k O_k E_k \quad (6)$$

In equation (6), $h_b = 14.876$, N_i indicates the number of times the first-level group i appears in the molecular structure, C_i is the first-order group contribution of type i , M_j indicates the number of times the second-level group j appears in the molecular structure, D_j is the second-order group contribution of type j , O_k indicates the number of times the third-level group k appears in the molecular structure, E_k is the third-order group contribution of type k . If using second and third order group contributions, $w = z = 1$, otherwise $w = z = 0$. Kolska, Ruzicka and Gani studied 589 different organic compounds. They reported the average relative error for estimation of enthalpy of vaporization at normal boiling temperature was 2.6% and the absolute average error was equal to 0.9 kJ/mol.

Group contribution methods usually are not dependent on other physical properties. To predict the enthalpy of vaporization at normal boiling temperature, the required information is limited to the chemical structure and geometry of the desired compound. However, group contribution methods compared to other methods (empirical methods) are very difficult to implement and using them requires a good knowledge of chemical structure. Also most group contribution methods have limited applications and do not include isomers; structural isomerism and especially spatial isomerism. Isomers are molecules with the same chemical formula but

Table 1
Group contribution of Joback and Reid method.

Group i	$(\Delta H_{vb})_i$	Group i	$(\Delta H_{vb})_i$
CH ₃ (1)	2.373	O (2)	2.41
CH ₂ (2)	2.226	O (ss) (2)	4.682
CH(3)	1.691	(C=O) (2)	8.972
C (4)	0.636	(C=O) (ss) (2)	6.645
(=CH ₂) (1)	1.724	(CH=O) (1)	9.093
(=CH) (2)	2.205	COOH(1)	19.537
(=C) (3)	2.138	COO(2)	9.633
(=C=) (2)	2.661	(=O) (1)	5.909
(≡CH) (1)	1.155	NH ₂ (1)	10.788
(≡C) (2)	3.302	NH(2)	6.436
CH ₂ (ss) (2)	2.398	NH(ss) (2)	6.930
CH(ss) (3)	1.942	N (3)	1.896
C (ss) (4)	0.644	(=N) (2)	3.335
(=CH) (ds) (2)	2.544	(=N) (ds) (2)	6.528
(=C) (ds) (3)	3.059	(=NH) (1)	12.169
F (1)	−0.67	C≡N (1)	12.851
Cl (1)	4.532	NO ₂ (1)	16.738
Br (1)	6.582	SH(1)	6.884
I (1)	9.520	S (2)	6.817
OH(1)	16.826	S (ss) (2)	5.984
ACOH(1)	12.499		

different chemical structures. In spatial isomerism, the bond structure is the same, but the geometrical position of the atoms and functional groups differs [16,17]. This difference should be considered in order to predict the enthalpy of vaporization at normal boiling temperature of different isomers.

The Joback and Reid method has a simple equation, which is enough to provide quantitative information about the structure of the compound to predict the enthalpy of vaporization at normal boiling temperature but the simplicity of the equation reduces the accuracy of the equation and increases the total error. On the other hand, the Kolska, Ruzicka and Gani method is more complex. The prominent feature of this method is the provision of third-order group contribution. Also, a large number of first-order and second-order group contributions were provided by this method makes it very complex and needs an almost complete knowledge of the chemistry of compounds. Finally, another important issue is that in most of these studies only a limited number of compounds (several hundred compounds) have been investigated and this cannot guarantee the completeness of the provided models.

It seems also possible to combine a comprehensive relationship based on group contribution method with other readily available properties such as molecular weight to present an equation for the prediction of the enthalpy of vaporization at normal boiling temperature of organic compounds. The new group contribution method presented in this study is based on this idea to upgrade the original Joback and Reid method to include more organic compounds including isomers especially spatial isomers and also combine it with other available thermodynamic properties to promote its accuracy.

1.1. The new method

Experimental data of the enthalpy of vaporization at normal boiling temperature were collected for 3950 unique organic compounds from the Yaws Handbook [18]. Correct input data play a key role for the successful model development. This Handbook is one of the most comprehensive sources of physical property data for chemical species.

These compounds were classified to the following groups: alkanes, cycloalkanes, alkenes, cycloalkenes, alkynes, benzene derivatives, aromatics, alcohols, phenols, ethers, ketones, aldehydes, esters, formates, acids, others C·H·O compounds, amines, other nitrogen compounds, sulfur compounds, chlorine compounds, fluorine compounds, bromine compounds, iodine compounds, other halogen compounds and other compounds. The number of the experimental data for each group of organic compounds are listed in the Table 2.

The first order group contribution method of Joback and Reid presented in Table 1 was used in this study. In order to generalize and avoid the limitations of the original Joback and Reid method, a number of new first-order group contributions were added to the original Joback and Reid method. Table 3 includes the list of these new group contributions.

Finally, Table 4 contains all of the first-order group contributions in the new method [19].

The notation of the table is such that when an atom is bonded to an element other than hydrogen, (1) means a single bond, (2) means 2 single bonds, = means a double bond and ≡ means a triple bond, (ss) or single site means that the group exists in a ring such as in naphthenics, (ds) or double site means that the group exists in a ring such as in aromatics and, AOH means that the OH is connected to the ring.

To solve the problem of the inability of the Joback and Reid method to predict the enthalpy of vaporization at normal boiling temperature of isomers, second-order group contributions were

Table 2

The list of compounds.

Components	Number of Components
Alkanes	338
Cyclo alkanes	124
Alkenes	270
Cyclo alkenes	62
Alkynes	81
Benzene derivatives	151
Aromatics	43
Alcohols	148
Phenols	37
Ethers	163
Ketones	152
Aldehydes	58
Esters	255
Formates	13
Acids	50
Others C·H·O compounds	68
Amines	174
Others nitrogen compounds	302
Sulfur compounds	149
Chlorine compounds	240
Fluorine compounds	78
Bromine compounds	122
Iodine compounds	33
Others halogen compounds	650
Others compounds	189

Table 3

First-order group contribution added to the original Joback and Reid method.

Group
OH (1) (Cyclic Alcohol)
HCOO (1) (Formate)
(C=O)-O-(C=O) (2) (Anhydride)
(C=O)-O-(C=O) (2) (ss) (Cyclic Anhydride)
N (ss) (3)
= C (ss) (3)
= S (1)
S=O (2)
S=O (ss) (2)
O=S=O (2)
O=S=O (ss) (2)

added to the original Joback and Reid method. It is also expected to increase the accuracy of the equation by adding the second-order group contributions. A list of second-order group contributions is presented in Table 5 [19].

According to Tables 4 and 5, the first-order and second-order group contributions were identified and recorded for all 3950 compounds in the collected data bank. The data bank which was established for this work contains information related to the name, chemical formula, compounds class, molecular weight, experimental enthalpy of vaporization at normal boiling temperature and the number of first-order and second-order group contributions of the organic compounds.

Selecting a constant value as a coefficient C and adding it to the terms of group contribution is one of the main problems of the relationship provided by Joback and Reid, because the studies show that this coefficient C is different for various organic compounds with different molecular values. Therefore, the coefficient C is introduced as a cubic function of molecular weight in the equation (7). The coefficients of the equation (5) are also a discrete function of molecular weight according to Table 6.

$$\Delta H_{vb} = C + \sum_i n_i (\Delta H_{vb})_i + \sum_j n_j (\Delta H_{vb})_j \quad (7)$$

$$C = a + bM_w + cM_w^2 + dM_w^3$$

Table 4

First-order group contributions in new method.

Group i	$(\Delta H_{vb})_i$	Group i	$(\Delta H_{vb})_i$
CH ₃ (1)	0.965	COO(2) (Ester)	0.696
CH ₂ (2)	1.792	(C=O)-O-(C=O) (2) (Anhydride)	4.285
CH(3)	1.717	(C=O)-O-(C=O) (2) (ss) (Cyclic Anhydride)	6.794
C (4)	1.502	(=O) (1)	-1.327
CH ₂ (ss) (2)	1.740	NH ₂ (1)	3.207
CH(ss) (3)	1.591	NH(2)	2.180
C (ss) (4)	0.924	NH(ss) (2)	2.616
= C (ss) (3)	1.192	N (ss) (3)	1.049
(=CH ₂) (1)	9.334e-06	N (3)	0.521
(=CH) (2)	1.839	(=N) (2)	9.206e-06
(=C) (3)	1.004	(=N) (ds) (2)	1.937
(=C=) (2)	2.905	C≡N (1)	6.564
(≡CH) (1)	0.609	NO ₂ (1)	2.542
(≡C) (2)	1.935	SH(1)	5.800
(=CH) (ds) (2)	2.262	S (2)	5.272
(=C) (ds) (3)	2.793	S (ss) (2)	5.330
OH(1)	4.485	= S (1)	5.533
OH (1) (Cyclic Alcohol)	3.618	S=O (2)	4.846
AOH(1) (Phenol)	2.473	S=O (ss) (2)	-0.006
O (2) (Ether)	-1.452	O=S=O (2)	0.332
O (ss) (2) (Ether)	-0.006	O=S=O (ss) (2)	0.421
(C=O) (2) (Ketone)	2.210	F (1)	-2.253
(C=O) (ss) (2) (Ketone)	5.050	Cl (1)	0.482
(CH=O) (1) (Aldehyde)	3.833	Br (1)	1.993
COOH(1) (Acid)	7.964	I (1)	0.001
HCOO (1) (Formate)	1.684		

In equation (7), n_i indicates the number of times the first-level group i appears in the molecular structure, $(\Delta H_{vb})_i$ is the first-order group contribution of type i , n_j indicates the number of times the second-level group j appears in the molecular structure, $(\Delta H_{vb})_j$ is the second-order group contribution of type j and M_w is the molecular weight of the desired compound. The parameters a , b , c , d are optimized for each molecular weight range and are presented in Table 6. The values $(\Delta H_{vb})_i$, $(\Delta H_{vb})_j$ are optimized values of the group contributions listed in the Tables 4 and 5. MATLAB software is used to optimize the parameters and coefficients of the equation using the fminsearch algorithm. Fminsearch is generally referred to as unconstrained nonlinear optimization. Fminsearch finds the minimum of objective function, starting at an initial estimate. Objective function is a scalar function of several variables. Fminsearch algorithm uses the Nelder-Mead simplex algorithm as described in Lagarias et al. [20]. This algorithm uses a simplex of $n+1$ points for n dimensional vectors X . The algorithm first makes a simplex around the initial guess X_0 by adding 5% of each component $X_0(i)$ to X_0 , and using these n vectors as elements of the simplex in addition to X_0 (It uses 0.00025 as component i if $X_0(i) = 0$). In this new method, the objective function is considered to be the percentage of average relative error (%ARE) according to the following equation:

$$\%ARE = \frac{1}{N} \sum_{k=1}^N 100 \times \left| \frac{\Delta H_{vbk}^{exp} - \Delta H_{vbk}^{cal}}{\Delta H_{vbk}^{exp}} \right| \quad (8)$$

In equation (8), ΔH_{vb}^{exp} is the experimental, ΔH_{vb}^{cal} is the calculated enthalpy of vaporization at normal boiling temperature and N is the number of data points.

2. Results and discussion

The predictions of the new model are compared to the experimental data in the Table 7. Different statistical measures including the percentage of average relative error (%ARE), average absolute error (AAE) and different range of the percentage relative error (%)

RE) and absolute error (AE) have been reported in this table. These errors are defined according to the following equations:

$$AE \text{ (kJ/mol)} = \left| \Delta H_{vb}^{exp} - \Delta H_{vb}^{cal} \right| \quad (9)$$

$$\%RE = 100 \times \left| \frac{\Delta H_{vb}^{exp} - \Delta H_{vb}^{cal}}{\Delta H_{vb}^{exp}} \right| \quad (10)$$

$$AAE \text{ (kJ/mol)} = \frac{1}{N} \sum_{k=1}^N \left| \Delta H_{vbk}^{exp} - \Delta H_{vbk}^{cal} \right| \quad (11)$$

One of the weak points of the published empirical correlations for different thermodynamic properties is the sole dependence on the correlative data. To say it in other words, the different coefficients of the empirical correlations are usually fitted with the aid of a set of experimental data which can be called the training set. If the same training set is used to test the accuracy of the presented model, the agreement is usually excellent but it cannot prove the prediction potential of the presented work as it is usually claimed by the researchers. This fact can only prove the correlative ability of the empirical correlation. To avoid this problem, a training set is selected to develop and optimize the different coefficients of the group contributions of the new. Another part of the experimental data bank has been selected randomly as the testing data. This set has been used for the validation of the new model. Usually, training sets give good predictions in comparison with the test sets, because the new model itself has been formed using these data, but this fact does not mean that the new model can be used in practical cases. Using testing data which is not used for the model development may prove the predictive ability of the new model. 90% of the data (3555 compounds) were included in the training set and 10% of the data (395 compounds) were included in the testing set. The original data were divided to these two sets randomly. The results of the new method for training and testing sets are included in Table 7.

The error analysis also shows that 94.83% of the compounds

Table 5
Second-order group contributions in new method.

Group j	Description	(ΔH_{vb}) _j
(CH ₃) ₂ CH-	Two methyl groups connected to the CH group in a chain.	0.101
CH ₃ (CH)<	One methyl group connected to the CH in a chain.	-4.986e-04
CH ₃ -CH ₂ (CH-CH ₃)-	One methyl group connected to the CH into CH ₃ -CH ₂ -CH in a chain.	0.112
(CH ₃) ₃ C<	Three methyl groups connected to the C in a chain.	-0.023
(CH ₃) ₂ C<	Two methyl groups connected to the C in a chain.	-0.109
CH ₃ -CH ₂ [C(CH ₃) ₂]-	Two methyl groups connected to the C into CH ₃ -CH ₂ -C in a chain.	0.158
CH ₃ -CH ₂ (C-CH ₃)<	One methyl group connected to the C into CH ₃ -CH ₂ -C in a chain.	0.592
CH ₃ (C)<	One methyl group connected to the C in a chain.	0.185
CH ₂ =CH-	One methylene group connected to the CH in a chain by a double bond.	0.355
CH ₂ =(C-CH ₃)-	One methyl group and one methylene group connected to the C in a chain by a double bond.	1.681
CH ₂ =C<	One methylene group connected to the C in a chain by a double bond.	1.243
CH ₃ -CH =	One methyl group connected to the CH = in a chain.	-0.307
CH ₃ -CH ₂ -CH =	One CH ₃ -CH ₂ group connected to the CH = in a chain.	-0.516
CH ₃ -CH ₂ (C-) =	One CH ₃ -CH ₂ group connected to the CH = in a chain.	1.040
CH ₃ -CH ₂ (C-CH ₃) =	One methyl group connected to the C = into CH ₃ -CH ₂ -C = in a chain.	1.208
CH ₃ (C-) =	One methyl group connected to the C = in a chain.	1.422
(CH ₃) ₂ C =	Two methyl groups connected to the C = in a chain.	0.679
CH≡C-	One methylidyne group connected to the C in a chain by a triple bond.	0.418
CH ₃ -C≡C-	One methyl group connected to the C≡C in a chain.	0.449
CH ₃ -CH ₂ -C≡C-	One CH ₃ -CH ₂ group connected to the C≡C in a chain.	-0.031
CH ₃ -O-	One methyl group connected to the oxygen atom in a chain.	1.503
CH ₃ -CH ₂ -O-	One CH ₃ -CH ₂ group connected to the oxygen atom in a chain.	0.572
(CH ₃) ₂ N-	Two methyl groups connected to the nitrogen atom in a chain.	0.550
CH _a - a ε (0–3)	One carbon atom connected to the main chain or ring, exclusive of the above foregoing functional groups (1–23).	0.023
CH ₃ CH _b - a,b ε (0–3)	Two carbon atoms connected to the main chain or ring, exclusive of the above foregoing functional groups (1–23).	0.120
CH ₄ CH ₆ CH _c -a,b,c ε (0–3)	Three carbon atoms connected to the main chain or ring, exclusive of the above foregoing functional groups (1–23).	-0.066
CH ₄ CH ₆ CH ₄ CH _d -a,b,c,d ε (0–3)	Four carbon atoms connected to the main chain or ring, exclusive of the above foregoing functional groups (1–23).	0.128
CH ₄ CH ₆ CH _c ... CH _d -a,b,c,d, ...ε (0–3)	The other groups higher than four carbon atoms, connected to the main chain or ring, exclusive of the above foregoing functional groups (1–23).	6.412e-08
N _{carbon}	Number of carbons into the other groups higher than four carbon atoms.	-0.074
Alkene bond	The alkene chain connected to the ring.	1.108
Ring	Number of ring.	-0.150
C-C	Number of the common single bonds between connected rings.	0.567
C=C	Number of the common double bonds between connected rings.	-0.149
C-C (out)	Number of the common single bonds between many rings.	-0.232
Double bond	Number of double bond.	0.024
Triple bond	Number of triple bond.	0.013
Cis-	Number of cis- position.	0.354
Trans-	Number of trans- position.	-4.030e-04
Alpha	Number of atoms into the alpha position, for cis hydrocarbons alpha is 2 and trans hydrocarbons alpha is 1.	-0.397
Beta	Number of atoms into the beta position, for cis hydrocarbons beta is 0 and trans hydrocarbons beta is 1.	-1.473e-06
C ₁ ring	All of the ring members must be numbered, the numbering begins from the side chain with lower carbon atoms into a clockwise and this is number of side chain on the first carbon atoms into the ring.	-0.226
C ₂ ring	Number of side chain on the second carbon atoms into the ring.	-0.006
C ₃ ring	Number of side chain on the third carbon atoms into the ring.	0.061
C ₄ ring	Number of side chain on the fourth carbon atoms into the ring.	0.061
C ₅ ring	Number of side chain on the fifth carbon atoms into the ring.	0.067
C ₆ ring	Number of side chain on the sixth carbon atoms into the ring.	0.098
C ₁ =C ₂	A double bond between first carbon and second carbon into the ring.	-0.958
C ₂ =C ₃	A double bond between second carbon and third carbon into the ring.	-1.268
C ₃ =C ₄	A double bond between third carbon and fourth carbon into the ring.	-1.481
C ₄ =C ₅	A double bond between fourth carbon and fifth carbon into the ring.	-1.273
C ₅ =C ₆	A double bond between fifth carbon and sixth carbon into the ring.	0.280
C ₆ =C ₁	A double bond between sixth carbon and first carbon into the ring.	0.105
C ₅ =C ₁	A double bond between fifth carbon and first carbon into the ring.	-1.697
Alpha-6	Number of side chain, oxygen, nitrogen and sulfur atoms in alpha position into the six membered ring of bicyclo compounds.	-0.278
Beta-6	Number of side chain, oxygen, nitrogen and sulfur atoms in beta position into the six membered ring of bicyclo compounds.	0.542
Gamma-6	Number of side chain, oxygen, nitrogen and sulfur atoms in gamma position into the six membered ring of bicyclo compounds.	0.330
Alpha-5	Number of side chain, oxygen, nitrogen and sulfur atoms in alpha position into the five membered ring of bicyclo compounds.	-0.563
Beta-5	Number of side chain, oxygen, nitrogen and sulfur atoms in beta position into the five membered ring of bicyclo compounds.	-0.192
Left ring side chain	Number of side chain, oxygen, nitrogen and sulfur atoms into the left ring of polycyclic compounds.	0.089
Right ring side chain	Number of side chain, oxygen, nitrogen and sulfur atoms into the right ring of polycyclic compounds.	0.328
Middle ring side chain	Number of side chain, oxygen, nitrogen and sulfur atoms into the middle ring of polycyclic compounds.	1.052
Left ring double bond	Number of double bond into the left ring of polycyclic compounds.	0.085
Right ring double bond	Number of double bond into the right ring of polycyclic compounds.	-0.107
Mid ring double bond	Number of double bond into the middle ring of polycyclic compounds.	-0.649

Table 5 (continued)

Group j	Description	$(\Delta H_{vb})_j$
Oxygen	Number of oxygen atoms.	1.910
Nitrogen	Number of nitrogen atoms.	1.062
Sulfur	Number of sulfur atoms.	−0.426
Chlorine	Number of chlorine atoms.	1.816
Fluorine	Number of fluorine atoms.	1.094
Bromine	Number of bromine atoms.	1.664
Iodine	Number of iodine atoms.	5.566

Table 6
Coefficients of Equation (7).

M_w	a	b	c	d
$M_w \leq 50$	4.851	0.285	−6.446e-04	1.045e-05
$50 < M_w \leq 70$	14.386	0.083	1.150e-06	−5.465e-07
$70 < M_w \leq 100$	18.352	0.050	−1.983e-04	−9.051e-08
$100 < M_w \leq 230$	16.224	0.073	−1.761e-04	−4.344e-08
$230 < M_w \leq 410$	15.791	0.061	−1.375e-04	9.587e-08
$M_w > 410$	14.341	0.061	−1.639e-04	3.701e-08

Table 7
The results of the new method.

	New Method	Training set	Testing set
Substances	3950	3555	395
%ARE	1.683	1.656	1.920
AAE (kJ/Mol)	0.620	0.610	0.704
%RE ≤ 1	1505	1378	127
1 < %RE ≤ 2	1064	955	109
2 < %RE ≤ 3	739	659	80
3 < %RE ≤ 4	438	388	50
%RE > 4	204	175	29
AE ≤ 5 kJ/mol	3945	3552	393
5 < AE ≤ 10	5	3	2

have the percentage of relative error (%RE) smaller or equal to 4 and only 0.12% of the compounds have absolute error (AE) greater than 5 kJ/mol. No compound was found to has a relative error higher

than 10%. The deviations of the new method for different types of organic compound classes are presented in the Table 8. For further and more accurate examination, the percentage of average relative error (%ARE), average absolute error (AAE) for different groups of compounds in the data bank are reported in Table 8. According to this table, the model predictions were in excellent agreement with the experimental data for all of the chemical families. Table 8 clearly shows that the deviations for different groups in the data bank are not very fluctuating, which indicates that the new method is accurate for all families of organic compounds.

Other methods were compared to the new model to detect any possible weaknesses of the new model. In Table 9, the new method was compared with the Joback and Reid and the Kolska, Ruzicka and Gani method. According to Table 9, the percentage of average relative error (%ARE) and average absolute error (AAE) of the new method are much lower than the Joback and Reid and the Kolska, Ruzicka and Gani method. According to Table 9, in the new method, 94.94% of the compounds have the percentage relative error (%RE) smaller or equal to 4 and also only 0.11% of the compounds have absolute error (AE) greater than 5 kJ/mol. However, this table also shows that for the Joback and Reid method, only 49.08% of the compounds have the percentage relative error (%RE) smaller or equal to 4 and also 16.18% of the compounds have absolute error (AE) greater than 5 kJ/mol. For Kolska, Ruzicka and Gani method, 44.20% of the compounds have the percentage relative error (%RE) smaller than or equal to 4 and also 20.32% of the compounds have absolute error (AE) greater than 5 kJ/mol. These results show that the new method seems to be more accurate compared to the

Table 8
The results of the new model for the different classes of organic compounds.

Components	Number of Components	Training set	Testing set	%ARE	AAE
Alkanes	338	34	304	1.410	0.537
Cyclo alkanes	124	12	112	1.849	0.628
Alkenes	270	28	242	1.569	0.500
Cyclo alkenes	62	6	56	1.540	0.527
Alkynes	81	8	73	2.041	0.664
Benzene derivatives	151	15	136	1.210	0.514
Aromatics	43	4	39	1.307	0.644
Alcohols	148	15	133	2.286	0.899
Phenols	37	3	34	1.682	0.769
Ethers	163	17	146	1.974	0.661
Ketones	152	15	137	1.535	0.604
Aldehydes	58	5	53	1.800	0.631
Esters	255	25	230	1.546	0.601
Formates	13	2	11	1.957	0.668
Acids	50	5	45	2.265	0.967
Others C-H-O compounds	68	8	60	1.423	0.586
Amines	174	17	157	1.786	0.679
Others nitrogen compounds	302	30	272	1.541	0.584
Sulfur compounds	149	15	134	1.455	0.542
Chlorine compounds	240	24	216	1.752	0.619
Fluorine compounds	78	8	70	2.399	0.645
Bromine compounds	122	12	110	1.718	0.622
Iodine compounds	33	4	29	1.465	0.530
Others halogen compounds	650	64	586	1.722	0.633
Others compounds	189	19	170	1.848	0.713

Table 9

The comparison of different methods.

Method	New Method	Joback and Reid	Kolska, Ruzicka and Gani
Substances	3459	3459	3459
%ARE	1.677	6.818	7.880
AAE (kJ/Mol)	0.615	2.750	3.202
%RE ≤ 1	1319	530	427
1 < %RE ≤ 2	936	447	429
2 < %RE ≤ 3	653	400	354
3 < %RE ≤ 4	376	321	319
%RE > 4	175	1761	1930
AE ≤ 5 kJ/mol	3455	2899	2756
5 < AE ≤ 10	4	446	518
10 < AE ≤ 15	0	63	125
15 < AE ≤ 20	0	25	24
AE > 20	0	26	36

original Joback and Reid and the Kolska, Ruzicka and Gani method.

The error analysis of the new method has been compared with the original Joback and Reid and the Kolska, Ruzicka and Gani method for different types of organic compounds in the Table 10. According to this table, for all of the organic compounds, the percentage of average relative error (%ARE) and average absolute error (AAE) of the new method is lower than that of the Joback and Reid or the Kolska, Ruzicka and Gani method. This fact clearly shows the higher accuracy of the new method comparing to other methods.

A comparison between the predictions of the new and the other

methods for isomeric compounds is presented in Table 11. Average absolute error (AAE) and the percentage of average relative error (%ARE) for the structural isomers, cis-isomers and the trans-isomers are reported in this table. The second-order group contributions defined in the new model are able to distinguish most isomers including cis- and trans-structures. The results clearly show that the new method is definitely more accurate than previous methods in predicting the enthalpy of vaporization at normal boiling temperature.

3. Conclusion

A new group contribution method is presented which is able to predict the enthalpy of vaporization at normal boiling temperature of organic compounds. The modification of the first-order group contributions, the addition of the second-order group contributions and the fundamental changes in the final equation of the original Joback and Reid method have led to an increase in the accuracy and the comprehensiveness. The new method is able to predict this property for a wide range of organic compounds. Also, by adding the second-order group contributions, the enthalpy of vaporization at normal boiling temperature of many isomers, especially spatial isomers is estimated with higher accuracy, while other methods are not able to distinguish between different isomers. The new method is also compared with the original Joback and Reid and the Kolska, Ruzicka and Gani method, and the results clearly indicate that this model is much more accurate.

Table 10

The results of different models for the different types of organic compounds.

Components	number of components	New method		Joback and Reid		Kolska, Ruzicka and Gani	
		AAE	%ARE	AAE	%ARE	AAE	%ARE
Alkanes	336	0.538	1.473	1.174	2.556	1.583	3.476
Cyclo alkanes	122	0.632	1.859	1.059	2.674	1.215	2.956
Alkenes	262	0.492	1.514	1.575	3.308	1.968	4.237
Cyclo alkenes	59	0.530	1.547	0.789	2.212	1.698	4.729
Alkynes	80	0.642	1.932	1.483	3.410	2.441	5.882
Benzene derivatives	148	0.515	1.215	3.217	5.635	3.788	6.844
Aromatics	43	0.644	1.307	1.693	3.271	3.874	7.374
Alcohols	113	0.920	2.352	8.072	21.108	7.472	19.599
Phenols	36	0.759	1.664	8.234	17.857	8.918	19.294
Ethers	157	0.664	1.981	1.088	3.224	1.964	5.522
Ketones	152	0.604	1.535	2.433	5.961	5.130	12.739
Aldehydes	58	0.631	1.800	1.319	3.492	2.029	5.414
Esters	231	0.598	1.547	3.330	8.146	4.279	10.474
Acids	43	0.982	2.317	5.177	11.668	3.447	7.747
Others C-H-O compounds	63	0.608	1.474	7.037	16.973	9.535	22.623
Amines	156	0.665	1.786	3.637	9.101	3.025	7.213
Others nitrogen compounds	200	0.568	1.518	5.152	13.396	5.286	13.495
Sulfur compounds	103	0.542	1.465	1.325	3.451	1.404	3.503
Chlorine compounds	236	0.617	1.747	1.339	3.561	1.358	3.767
Fluorine compounds	74	0.618	2.265	2.290	8.849	2.036	7.716
Bromine compounds	122	0.622	1.718	1.464	3.956	1.498	4.136
Iodine compounds	33	0.530	1.465	0.963	2.445	0.841	2.142
Others halogen compounds	553	0.638	1.732	3.341	8.636	3.727	9.625
Others compounds	79	0.789	2.110	4.079	9.757	4.208	10.051

Table 11

A comparison of the different models for hydrocarbon isomers.

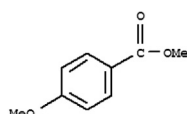
Components	New method			Joback and Reid method			Kolska, Ruzicka and Gani method		
	Number	AAE(kJ/Mol) (KJ/Mol)	%ARE	Number	AAE(kJ/Mol) (KJ/Mol)	%ARE	Number	AAE(kJ/Mol) (KJ/Mol)	%ARE
structural isomers	2710	0.623	1.676	2710	2.492	6.380	2710	2.877	7.330
cis isomers	168	0.478	1.455	168	1.345	3.814	168	1.835	5.159
trans isomers	172	0.532	1.604	172	1.575	4.270	172	1.918	5.237

Example 1. Estimation of the enthalpy of vaporization at normal boiling temperature of 4,4-dimethyl-cis-2-pentene (experimental value: $\Delta H_{vb}^{exp} = 29.423$ kJ/mol, $M_W = 98.186$, C_7H_{14}).



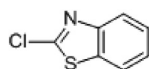
First-order groups	Occurrences	$n_i(\Delta H_{vb})_i$	second-order groups	Occurrences	$n_j(\Delta H_{vb})_j$
CH ₃ (1)	4	3.860	(CH ₃) ₂ C<	1	−0.023
C (4)	1	1.502	CH ₃ -CH =	1	−0.307
(=CH) (2)	2	3.678	Double bond	1	0.024
			Cis-	1	0.354
			Alpha	2	−0.794
Parameter	a	b	c	d	
70 < $M_W \leq 100$	18.352	0.050	−1.983e-04	−9.051e-08	
ΔH_{vb}^{exp}	ΔH_{vb}^{cal}		AE		%RE
29.423	29.549		0.126		0.428

Example 2. Estimation of the enthalpy of vaporization at normal boiling temperature of methyl 4-methoxybenzoate (experimental value: $\Delta H_{vb}^{exp} = 45.534$ kJ/mol, $M_W = 166.174$, $C_9H_{10}O_3$).



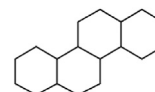
First-order groups	Occurrences	$n_i(\Delta H_{vb})_i$	second-order groups	Occurrences	$n_j(\Delta H_{vb})_j$
CH ₃ (1)	2	1.930	CH ₃ -O-	2	3.006
(=CH) (ds) (2)	4	9.048	Ring	1	−0.150
(=C) (ds) (3)	2	5.586	Double bond	4	0.096
O (2) (Ether)	1	−1.452	C ₁ ring	1	−0.226
COO(2) (Ester)	1	0.696	C ₄ ring	1	0.061
			C ₂ =C ₃	1	−1.268
			C ₄ =C ₅	1	−1.273
			C ₆ =C ₁	1	0.105
			Oxygen	3	5.730
Parameter	a	b	c	d	
100 < $M_W \leq 230$	16.224	0.073	−1.761e-04	−4.344e-08	
ΔH_{vb}^{exp}	ΔH_{vb}^{cal}		AE		%RE
45.534	45.191		0.343		0.753

Example 3. Estimation of the enthalpy of vaporization at normal boiling temperature of 2-chlorobenzothiazole (experimental value: $\Delta H_{vb}^{exp} = 45.920$ kJ/mol, $M_W = 169.632$, C_7H_4ClNS).



First-order groups	Occurrences	$n_i(\Delta H_{vb})_i$	second-order groups	Occurrences	$n_j(\Delta H_{vb})_j$
(=CH) (ds) (2)	4	9.048	Ring	2	−0.300
(=C) (ds) (3)	3	8.379	C=C	1	−0.149
(=N) (ds) (2)	1	1.937	Double bond	4	0.096
S (ss) (2)	1	5.330	C ₂ ring	1	−0.006
Cl (1)	1	0.482	C ₃ ring	1	0.061
			C ₄ ring	1	0.061
			C ₁ =C ₂	1	−0.958
			C ₃ =C ₄	2	−2.962
			C ₅ =C ₆	1	0.280
			Alpha-5	2	−1.126
			Beta-5	1	−0.192
			Left ring side chain	3	0.267
			Left ring double bond	1	0.085
			Right ring double bond	3	−0.321
			Nitrogen	1	1.062
			Sulfur	1	−0.426
			Chlorine	1	1.816
Parameter	a	b	c	d	
100 < $M_W \leq 230$	16.224	0.073	−1.761e-04	−4.344e-08	
ΔH_{vb}^{exp}	ΔH_{vb}^{cal}		AE		%RE
45.920	45.797		0.123		0.268

Example 4. Estimation of the enthalpy of vaporization at normal boiling temperature of octadecahydrochrysene (experimental value: $\Delta H_{vb}^{exp} = 56.127$ kJ/mol, $M_W = 246.431$, $C_{18}H_{30}$).



First-order groups	Occurrences	$n_i(\Delta H_{vb})_i$	second-order groups	Occurrences	$n_j(\Delta H_{vb})_j$
CH ₂ (ss) (2)	12	20.88	Ring	4	−0.600
CH(ss) (3)	6	9.546	C-C	3	1.701
Parameter	a	b	c	d	
230 < $M_W \leq 410$	15.791	0.061	−1.375e-04	9.587e-08	
ΔH_{vb}^{exp}	ΔH_{vb}^{cal}		AE		%RE
56.127	55.376		0.751		1.339

List of symbols

R	Universal gas constant
n_i, N_i	Number of times the first-level group i
n_j, M_j	Number of times the second-level group j
O_k	Number of times the third-level group k
$(\Delta H_{vb})_i$	C_i First-order group contribution of type i
$(\Delta H_{vb})_j$	D_j Second-order group contribution of type j
E_k	Third-order group contribution of type k
M_W	Molecular weight
N_C	Total number of carbon atoms
a, b, c	and d Adjustable parameters

<i>T</i>	Absolute Temperature
<i>P</i>	Pressure
<i>Z</i>	Compressibility coefficient
<i>H</i>	Enthalpy
<i>AE</i> (kJ/mol)	Absolute error
% <i>RE</i>	Percentage of relative error
<i>AAE</i> (kJ/mol)	Average absolute error
% <i>ARE</i>	Percentage of average relative error

Subscripts

<i>c</i>	Critical
<i>v</i>	Vaporization
<i>b</i>	Boiling
<i>r</i>	Reduced
<i>exp</i>	Experimental
<i>cal</i>	Calculated

References

- [1] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, *The Properties of Gases and Liquids*, 5nd Edition, McGraw-Hill, New York, 2001.
- [2] D. Aboali, M. Sobati, Novel method for prediction of normal boiling point and enthalpy of vaporization at normal boiling point of pure refrigerants: a QSPR approach, *Sci. Technol. Humanit.* 40 (2014) 282–293.
- [3] Z. Kolska, M. Zabransky, A. Randova, Group contribution methods for estimation of selected physico-Chemical properties of organic compounds, in: *Thermodynamics-Fundamentals and Its Application in Science*, InTech, 2012.
- [4] F. Gharagheizi, O. Babaie, S. Mazdeyasna, Prediction of vaporization enthalpy of pure compounds using a group contribution-based method, *Ind. Eng. Chem.* 50 (2011) 6503–6507.
- [5] L. Riedel, Eine neue universelle Dampfdruckformel Untersuchungen über eine Erweiterung des Theorems der übereinstimmenden Zustände. Teil I, *Chem. Ing. Tech.* 26 (1954) 83–86.
- [6] N.H. Chen, Generalized correlation for latent heat of vaporization, *J. Chem. Eng. Data* 10 (2) (1965) 207–210.
- [7] A. Vetere, New Generalized Correlations for Enthalpy of Vaporization of Pure Compounds, *Laboratori Ricerche Chimica Industriale*, San Donato Milanese, 1973.
- [8] I. Cachadina, A. Mulero, Evaluation of correlations for prediction of the normal boiling enthalpy, *Fluid Phase Equil.* 240 (2006) 173–178.
- [9] Q. Jia, Q. Wang, P. Ma, Prediction of the enthalpy of organic compounds at their normal boiling point with the positional distributive contribution method, *J. Chem. Eng. Data* 55 (2010) 5614–5620.
- [10] Z. Kolska, V. Ruzicka, R. Gani, Estimation of the enthalpy of vaporization and the entropy of vaporization for pure organic compounds at 298.15 K and at normal boiling temperature by a group contribution method, *Ind. Eng. Chem. Res.* 44 (2005) 8436–8454.
- [11] K.G. Joback, R.C. Reid, Estimation of pure-Component properties from group-contributions", *Chem. Eng. Commun.* 57 (1987) 233–243.
- [12] L.R. Constantinou, R. Gani, New group contribution method for estimating properties of pure compounds, *AIChE J.* 40 (10) (1994) 1697–1710.
- [13] J. Marrero, R. Gani, Group-contribution based estimation of pure component properties, *Fluid Phase Equil.* 183–184 (2001) 183–208.
- [14] G. Di Nicola, M. Falone, M. Pierantozzi, R. Stryjek, An improved group contribution method for the prediction of second virial coefficients, *Ind. Eng. Chem.* 53 (35) (2014) 13804–13809.
- [15] R.L. Gardas, J.A.P. Coutinho, A group contribution method for heat capacity estimation of ionic liquids, *Ind. Eng. Chem.* 47 (15) (2008) 5751–5757.
- [16] R.H. Petrucci, R.S. Harwood, F.G. Herring, *General Chemistry: Principles and Modern Applications*, 8nd Edition, Prentice-Hall, 2002, p. 91.
- [17] S.J. Gorzynski, *General, Organic and Biological Chemistry*, 1nd Edition, The McGraw-Hill Companies, 2010, p. 450.
- [18] C. Yaws, *Handbook of Thermophysical Properties of Chemicals and Hydrocarbons*, second ed., Gulf Professional, 2014.
- [19] H. Ghasemitabar, K. Movagharnjad, Estimation of the normal boiling point of organic compounds via a new group contribution method, *Fluid Phase Equil.* 411 (2016) 13–23.
- [20] J.C. Lagarias, J.A. Reeds, M.H. Wright, P.E. Wright, Convergence properties of the Nelder-Mead simplex method in low dimensions, *Society for Industrial and Applied Mathematics* 9 (1) (1998) 112–147.