

Predicting the Entropy of Boiling for Organic Compounds

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Received June 7, 1999

This study aims to predict the entropy of boiling (ΔS_b) for organic compounds by considering parameters that are indicative of both molecular geometry and molecular association. The proposed method is a modification of Trouton's rule. It utilizes three geometric parameters, σ , τ , and ω , that address molecular symmetry, flexibility, and planarity, respectively, as well as a set of group contributors that focus on hydrogen-bonding and strong dipolar interactions. The molecular geometry parameters are unique in that they reflect the ordering of molecules in the liquid that cannot be described by group contribution. The database of 903 organic compounds covers a broad array of structural categories. The root mean square error for the prediction is 2.12 J/mol·K, which is very low given the diversity of the database. An independent entropy dataset of 31 compounds was used to show that the proposed method is more accurate than four published methods. The success of this approach illustrates the need for nonadditive structural parameters along with group additive parameters to characterize phase change entropy.

INTRODUCTION

The entropy of vaporization at the normal boiling point, i.e., the entropy of boiling (ΔS_b), is an important property in chemical engineering and environmental sciences. A variety of methods have been reported to predict its value for organic compounds. Of these, the simplest and the most recognized is Trouton's rule in which ΔS_b is expressed as a constant, 88 J/mol·K;¹ Kistiakowsky² utilized the Clapeyron equation and the ideal gas law to derive an equation that correlates the entropy of boiling with the boiling point. The results generated substantially verified Trouton's observation; Fishtine³ modified Kistiakowsky's rule by applying correction factors with values that are based on the type of compounds and the length of the hydrocarbon chain; Vetere⁴ expressed ΔS_b as a function of the normal boiling point and the molar mass (M); Mishra and Yalkowsky⁵ modified Trouton's rule for long-chain hydrocarbons by incorporating the chain length into the equation to adjust the fact that the conformational freedom of flexible compounds is less in the liquid than in the gas; Myrdal et al.⁶ modified Trouton's rule by considering both hydrogen bonding and molecular flexibility. The latter is represented by the effective number of unrestricted torsional angles (τ). Recently group contribution methods were reported by Ma and Zhao⁷ and Hoshino et al.⁸ in which ΔS_b is calculated as the summation of contributions (ΔS_i) from the individual molecular fragments that constitute a compound. The former yielded better results due to the greater specificity of the substituents of its molecular breakdown scheme (96 group contributors).

The proposed method combines the above-mentioned three geometric parameters with group contribution values that reflect intermolecular association. The new equation will then be compared for its prediction accuracy with other available

methods by using an independent entropy dataset, i.e., the test set.

BACKGROUND

Entropy of Boiling. The entropy of boiling is a state quantity that yields information on the change in internal order of the molecules in the system. According to Boltzmann's statistical definition,⁹ the entropy of a phase is related to the logarithm of the number of ways (W) it can be achieved by its component molecules. The entropy of boiling ΔS_b is therefore proportional to the ratio of the number of ways in which the gas and the liquid can be achieved, i.e.

$$\Delta S_b = k \ln(W_{\text{gas}}/W_{\text{liquid}}) \quad (1)$$

where k is Boltzmann's constant ($k = 1.381 \times 10^{-23}$ J/K).

The entropy of boiling can also be described as a sum of translational, rotational, and conformational components:¹⁰

$$\Delta S_b = \Delta S_{\text{translational}} + \Delta S_{\text{conformational}} + \Delta S_{\text{rotational}} \quad (2)$$

According to Hildebrand,¹¹ any factor tending to produce order in a liquid would increase the entropy of the transition to vapor. The factors that produce order in a liquid may be classified as hydrogen bonding, dipole orientation, and geometrical shape. On the basis of this rationale, we will attempt to extend the prediction of the entropy of boiling to a broad range of organic compounds.

In a previous report,¹² we found that the entropy of boiling ΔS_b (J/mol·K) for hydrocarbons can be successfully predicted by the following modification of Trouton's rule:

$$\Delta S_b = 83.75 - 0.11\sigma + 0.51\tau + 0.05\omega^2 \quad (3)$$

where σ , τ , and ω represent the molecular rotational symmetry number, the effective number of torsional angles, and the molecular planarity number, respectively. The

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equation was generated by multiple regression on a database of 477 hydrocarbons.

Symmetry. Dannenfelser and Yalkowsky¹³ defined the molecular rotational symmetry number, σ , as the number of identical images that can be produced by rigid rotation of a hydrogen-suppressed molecule. The value of σ is always equal to or greater than unity since every molecule has at least one identical orientation produced by a 360° rotation about any axis. On the basis of this definition, the σ values are 2 for toluene and *o*-xylene, 3 for chloroform and methanol, 4 for *p*-xylene and naphthalene, 6 for 1,3,5-trimethylbenzene and 1,3,5-trichlorobenzene, and 12 for benzene and carbon tetrachloride. Methane, a spherically shaped molecule, has an infinite number of infinite rotational axes, and σ is empirically assigned a value of 100. Cylindrical molecules such as propadiene, ethane, ethyne, and carbon dioxide which have one infinite rotational axis are empirically assigned a σ value of 20. Conical molecules such as hydrogen cyanide and carbon monoxide are assigned a σ value of 10.

Although the symmetry number, σ , is not a molecular shape descriptor, it tends to be correlated with molecular sphericity and/or roundness. Symmetrical molecules are more likely to rotate with less expansion than nonsymmetrical molecules. A more freely rotating molecule in the liquid has a higher degree of entropy due to the increased rotational disorder, and hence a smaller entropy change upon vaporization.

Flexibility. The conformational freedom, or flexibility, of a molecule arises from the ability of its atoms to torsionally rotate about single bonds. Dannenfelser and Yalkowsky¹³ developed the following empirical calculation of the effective number of torsional angles, τ :

$$\tau = \text{SP3} + 0.5(\text{SP2}) + 0.5(\text{RING}) - 1 \quad (4)$$

where SP3 is the number of nonring, nonterminal, sp³ atoms (including NH, N, O, and S), SP2 is the number of nonring, nonterminal, sp² atoms, and RING is the number of monocyclic or fused ring systems in the molecule. Hydrogen atoms, sp carbon atoms, and terminal groups such as -CH₃, -NH₂, -OH, and -Cl are ignored because they do not contribute to molecular flexibility. The *tert*-butyl group -C(CH₃)₃ and trihalomethyl group CX₃ are each treated as a single terminal group since their rotation does not add substantially to the flexibility. For example, *n*-pentane, 1-chlorobutane, diethyl ether, diisopropyl ether, diethylamine, 2,4-hexanedione, phenyl propyl ketone, and benzocaine all have τ values of 2. The value of τ is set to zero if the calculation yields a negative value.

ΔS_b , or the entropy of boiling, is expected to rise with an increase in the molecular τ value because this translates to the higher conformational freedom upon vaporization. This is consistent with its positive coefficient in eq 3.

Planarity. The molecular planarity number, ω , described by Zhao et al.¹² is the number of non-hydrogen atoms of a molecule that are restricted to a single plane. Methane and ethane have ω values of 1 and 2, respectively. All other alkanes have ω values of 3. All conjugated atoms are assumed to be coplanar. For example, the ω values for butadiene, benzene, styrene, naphthalene, and anthracene are 4, 6, 8, 10, and 14, respectively. Atoms adjacent to double

and/or triple bond(s) are of necessity in the same plane as the atoms of the bond. Therefore, 2,3,4-trimethyl-2-pentene has an ω value of 6. Similarly atoms adjacent to an aromatic ring are coplanar with the ring, and the ω values are 7 for phenol, toluene, and aniline and 9 for benzoic acid, 1,3,5-trimethylbenzene, and *p*-hydroxybenzaldehyde.

Experimental data indicate that planar aromatics, and fused-ring aromatics in particular, deviate from Trouton's rule. It is likely that these flat molecules are partially stacked in the liquid. The increased level of molecular ordering or layering reduces the liquid entropy and thus increases the entropy of boiling, giving ω a positive coefficient in eq 3.

Group Contributors. Hydrogen bonding is the single most important factor that causes the entropy of boiling to deviate substantially from Trouton's rule. This is because hydrogen bonding is very directional and produces partial alignment in the liquid. For example, hydrogen fluoride and 4-hydroxybenzaldehyde tend to form a loose chainlike structure in the liquid state.¹⁴ When the liquid goes into the gas state, the alignment is disrupted, and gives rise to an increase in the entropy change upon vaporization, i.e., ΔS_b is increased. The proposed method considers most recognized hydrogen-bonding groups including aliphatic acids (RCOOH), aromatic acids (ArCOOH), alcohols (ROH), phenols (ArOH), primary amines (RNH₂), secondary amines (RR'NH), anilines (ArNH₂), and thiols (RSH). Although amides are important, they are not included due to a lack of experimental data. Strong dipole-dipole interactions were also found to cause deviation from Trouton's rule.

EXPERIMENTAL SECTION

Data. The entropy data of 934 compounds used in this study were taken from reported values of the heat of vaporization at the normal boiling point.¹⁵⁻²⁰ These entropy data cover a broad range of organic compounds: alkanes, alkenes, alkynes, dienes, cycloalkanes, alkylaromatics, halides, esters, ethers, thiol ethers, ketones, alcohols, phenols, carboxylic acids, amines, thiols, disulfides, thioesters, etc. Microsoft Excel vision 97 was used to randomize the data into 30 portions. Twenty-nine portions (903 compounds) were used as the training set for equation generation, and the remaining portion (31 compounds) was used as the test set to evaluate the proposed method and other available methods.

Statistical Analysis. The entropy database was compiled in WindowDbase 95 and was analyzed by the statistical analysis system (SAS). The multiple regression model held the entropy of boiling as a dependent variable and all molecular parameters and group contributors as independent. The root mean square error (RMSE) was used to measure the predictive ability of the proposed model. The *T* value was used to determine the significance of each individual molecular parameter toward the whole equation developed. The *T* value can be calculated from the ratio of the parameter coefficient over the standard error (SE). The coefficient with a *T* value of more than 3.5 is considered to be statistically significant (i.e., above the confidence level). The average absolute error (see the definition in Table 3) was used to compare the prediction accuracy among different methods. It was also used in the cross-validation of the proposed model.

Table 1. Group Contributor, Coefficient, and Occurrence

group contributor	coeff $X_i \pm$ SE (J/mol·K)	occurrence	group contributor	coeff $X_i \pm$ SE (J/mol·K)	occurrence
aliphatic acid (RCOOH)	19.9 \pm 1.0	5	ester (RCOOR')	3.7 \pm 0.4	38
alcohol (ROH)	19.1 \pm 0.3	59	thiol ester (RCOSR')	3.0 \pm 1.0	4
hydrazine (RNHNHR')	12.9 \pm 1.2	3	ketone (RCOR')	2.9 \pm 0.5	19
phenol (ArOH)	12.8 \pm 0.3	58	secondary amine (RR'NH)	2.5 \pm 0.7	11
aromatic acid (ArCOOH)	8.6 \pm 2.1	1	thiol (RSH)	2.4 \pm 0.4	35
primary amine (RNH ₂)	5.8 \pm 0.4	30	nitrile (RCN)	2.2 \pm 0.6	15
aniline (ArNH ₂)	5.4 \pm 0.6	12	thiol ether (RSR')	2.0 \pm 0.4	31
disulfide (RSSR')	4.8 \pm 0.9	6	ether (ROR')	1.4 \pm 0.2	116
nitro (RNO ₂)	4.4 \pm 0.5	5			

Table 2. Selected Examples Illustrating Input Parameters, Observed ΔS_b , and Predicted ΔS_b

compound	σ	τ	ω	$n_i X_i$	ΔS_b (J/mol·K)	
					obsd	pred
methane	100	0	1	0	73.0	73.6
ethane	20	0	2	0	79.7	82.5
neopentane	12	0	3	0	80.4	83.7
cyclopropane	6	0	3	0	83.4	84.3
isobutane	3	0	3	0	81.5	84.7
propane	2	0	3	0	82.3	84.8
benzene	6	0	6	0	87.1	85.7
1,4-dimethylbenzene	4	0	8	0	87.4	87.3
1,2,4,5-tetramethylbenzene	4	0	10	0	90.1	89.1
naphthalene	4	0	10	0	88.1	89.1
phenanthrene	2	0	14	0	90.8	94.1
pyrene	4	0	16	0	98.8	96.9
chrysene	2	0	18	0	96.5	100.5
1-hexanethiol	1	4	3	2.4	87.4	88.7
1-heptanethiol	1	5	3	2.4	88.2	89.0
1-octanethiol	1	6	3	2.4	89.6	89.4
1-nonanethiol	1	7	3	2.4	90.1	89.7
1-decanethiol	1	8	3	2.4	90.6	90.1
methanol	3	0	2	19.1	104.2	103.5
1-heptanol	1	5	3	19.1	103.3	105.7
1,3-butanediol	1	2	3	38.2	121.7	123.8
1-amino-2-propanol	1	1	3	24.9	106.9	110.1
1,2-ethanediamine	1	1	3	11.6	97.3	96.8
phenol	2	0	7	12.8	100.3	99.6
<i>p</i> -toluidine	2	0	8	5.4	94.5	92.9
<i>n</i> -valeric acid	1	2.5	4	19.9	108.6	106.0
diglycol <i>n</i> -hexyl ether	1	11	3	21.9	108.1	110.6

RESULTS AND DISCUSSION

The relationship between the entropy of boiling ΔS_b (J/mol·K) and the molecular parameters was found by multiple regression on 903 compounds to be

$$\Delta S_b = 84.53 - 0.11\sigma + 0.35\tau + 0.05\omega^2 + \sum n_i X_i \quad (5)$$

where n_i is the occurrence of group i in the compound and X_i is the contribution of group i to the entropy of boiling. The low RMSE of 2.12 J/mol·K indicates that the proposed method has a high prediction accuracy given the diversity of the database. The SE for the intercept is extremely small: ± 0.14 . The standard errors for σ , τ , and ω are also small: ± 0.019 , ± 0.024 , and ± 0.002 , respectively. The SEs for 17 group contributors are shown in Table 1. The calculated T values are greater than 3.5 for all molecular parameters except one (RCOSR', which has a T value of 2.78). The overall F value for the model is 366.7, and the average absolute error is 1.5 J/mol·K.

It is seen that the intercept is very close to Trouton's rule (88 J/mol·K), which can be attributed to the fact that the gain in translational freedom of all molecules upon vaporiza-

tion is the major determinant of ΔS_b . The values of the geometric parameters in eq 5 are very close to those in eq 3. The coefficients for the 17 group contributors are listed in Table 1. Note that three of the group contributors (aromatic acid, hydrazine, and thiol ester) were based on an occurrence of less than 5.

The molecular rotational symmetry number, σ , was originally developed to predict the entropy of melting. It represents the probability of the molecule being in the correct orientation to fit into the crystal lattice. This concept is also appropriate for the entropy of boiling because the most symmetrical molecules tend to be nearly conical, cylindrical, or spherical. They therefore rotate more freely in the liquid with less expansion than do asymmetrical molecules. The greater degree of rotational disorder for symmetrical molecules in the liquid phase leads to a smaller entropy change upon transition to the vapor. Table 2 lists some experimental ΔS_b values for small molecules of varying symmetry numbers. Since τ and ω are similar for these compounds, the effect of molecular symmetry, σ , on the entropy of vaporization is clearly evident. Because the virtually spherical methane molecule is in complete orientational disorder in both the liquid and the gas phases, the rotational component to its entropy of boiling is nearly zero.

Dannenfels and Yalkowsky¹³ defined the molecular flexibility number ϕ as 2.85 raised to the power τ ($\phi = 2.85^\tau$) where τ is the effective number of torsional angles in a molecule as given by eq 4. The greater the number of conformations a molecule can assume, the greater its probability of existing as a liquid. The same concept can be applied in the entropy of boiling. Since a molecule is more conformationally restricted in the liquid than in the gas, ΔS_b must increase with increasing molecular flexibility. An approximately linear correlation of τ with ΔS_b is evident in data for the homologous series including *n*-alkanes, *n*-alkenes, *n*-alkylbenzenes,¹² and *n*-alkanethiols listed in Table 2.

Planar aromatic compounds and fused-ring aromatics in particular show deviations from Trouton's rule as seen in Table 2. It is speculated that their flat shape leads to a greater degree of intermolecular alignment and partial stacking of the molecules in the liquid. The increased order of the aligned molecules reduces the liquid entropy, and thus increases the entropy change upon boiling. The planarity number, ω , accounts for the alignment of flat molecules in the liquid phase. The larger the planar aromatic region, the greater the layering and thus ordering of the molecules in the liquid.

Table 1 lists the coefficients of the various molecular constituents. Alcohols and carboxylic acids have particularly larger coefficients since they form intermolecular hydrogen-

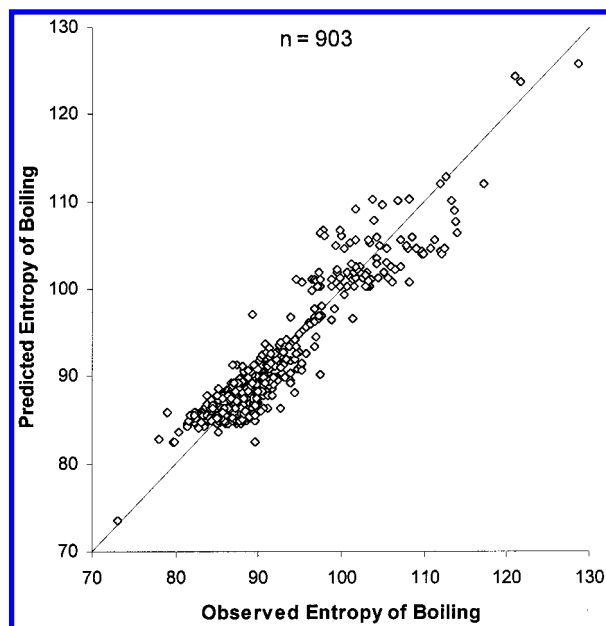


Figure 1. Observed versus predicted entropy of boiling, ΔS_b (J/mol·K).

bonded structures that restrict both rotational and conformational freedom of these compounds in the liquid state. Carboxylic acids can be strongly associated as chains or dimers stabilized by reinforced intermolecular hydrogen bonds primarily in the liquid. This self-association in the liquid leads to an increase in ΔS_b .

Table 1 also shows that weak hydrogen-bonding groups such as secondary amines and thiols contribute less than alcohols and acids to ΔS_b and that the coefficients of dipolar groups are even smaller.

Note that the volatile formic and acetic acids dimerize in the gas phase as well as in the liquid phase. This dimerization effectively increases the molecular weight of the evaporating substance and decreases the entropy calculated on the basis of its empirical formula weight. This self-association causes formic acid and acetic acid to have lower ΔS_b values than non-hydrogen-bonding compounds. Since such extensive dimerization is not observed for larger carboxylic acids, the two small acids were deleted from the final regression.

The proposed method does not cover compounds that can form intramolecular hydrogen bonds between adjacent strong hydrogen-bonding groups ($-\text{OH}$ and $-\text{OH}$, $-\text{OH}$ and $-\text{COOH}$, $-\text{COOH}$ and $-\text{CO}-$, etc.). These experimental data are very limited, and it is difficult to separate the effect of intermolecular and intramolecular interactions.

The observed versus predicted entropy of boiling data are shown in Figure 1 along with the line of identity. A large number of data for hydrocarbons are clustered in the 83–92 J/mol·K range. Hydrogen-bonding compounds are typically in the 95–115 J/mol·K range. Although the latter data are more scattered than the former, the overall agreement between the observed and predicted values is quite good.

Table 3. Comparison of Prediction Results for a Test Set of 31 Entropy of Boiling Data

name	ΔS_b (J/mol·K): obsd vs pred					
	obsd	Trouton ¹	Kristiakosky ²	Ma/Zhao ⁷	Myrdal ⁶	proposed
2,2,4-trimethylhexane	86.5	88.0	86.4	83.1	86.8	85.6
<i>p</i> -cresol	99.9	88.0	87.8	98.7	99.1	100.4
1,2,4-trimethylbenzene	88.7	88.0	87.3	88.6	86.0	88.4
diglycol methyl ether	108.3	88.0	87.7	97.7	99.8	108.5
1,3-propanediamine	98.9	88.0	86.7	98.8	95.7	97.2
<i>n</i> -eicosane	93.2	88.0	90.0	87.4	92.8	90.8
benzyl alcohol	105.6	88.0	87.9	109.7	99.3	106.2
isopropylamine	91.2	88.0	84.2	91.0	93.9	90.7
tridecylamine	94.2	88.0	89.0	93.4	92.8	94.6
methyl butanoate	89.9	88.0	85.9	91.3	87.4	90.1
2-methyl-2,4-pentanediol	121.6	88.0	87.8	128.5	103.8	123.8
glycol methyl ether	108.4	88.0	86.4	110.0	105.5	106.1
isobutylamine	89.8	88.0	85.1	91.2	92.8	91.1
anthracene	92.0	88.0	90.0	89.9	86.0	93.9
3-methyl-2-butanethiol	88.5	88.0	86.0	86.2	86.4	87.7
<i>sec</i> -butyl alcohol	109.3	88.0	85.8	106.3	105.6	104.3
2-methyl-2-heptene	86.7	88.0	86.3	86.7	87.2	86.7
2-methyl-2-butanol	104.0	88.0	85.9	104.8	102.5	104.3
<i>p</i> -propylphenol	102.3	88.0	88.4	99.3	97.0	101.0
isopentane	82.0	88.0	84.1	84.1	86.4	85.2
3-ethylheptane	88.3	88.0	86.7	84.8	88.0	86.6
<i>tert</i> -butylcyclohexane	83.2	88.0	87.3	82.7	86.4	85.2
4,4-dimethyl- <i>cis</i> -2-hexene	87.3	88.0	86.0	85.0	86.8	85.9
3-methyl-1-butyne	87.3	88.0	84.0	87.9	86.0	85.2
1,2-dibromo-2-methylpropane	86.3	88.0	86.9	86.4	86.0	84.9
isopropyl propyl sulfide	86.6	88.0	86.5	86.6	87.2	87.9
ethyl propyl ether	86.0	88.0	85.0	87.3	87.2	87.3
tetrahydrofuran	87.9	88.0	85.0	88.3	86.0	86.3
1-octanol	100.0	88.0	87.7	107.3	99.3	106.1
morpholine	93.8	88.0	86.5	94.9	86.0	88.8
<i>n</i> -hexylcyclopentane	86.4	88.0	87.9	85.2	87.8	86.5
av absolute error ^a		7.4	7.8	2.2	3.1	1.6

^a Av absolute error = $\sum |\Delta S_b^{\text{obsd}} - \Delta S_b^{\text{pred}}|/n$.

Table 4. Cross-Validation Results

cross-validation	RMSE for the training set (J/mol·K)	no. for the training set	av absolute error for the test set (J/mol·K)	no. for the test set
1	2.27	813	1.6	90
2	2.18	813	1.5	90
3	2.08	813	1.5	90

COMPARISON WITH PUBLISHED CALCULATION METHODS

A test set of data of 31 randomly selected compounds was used to evaluate the prediction accuracy of the proposed method and other available methods. The results are given in Table 3. The average absolute error for the proposed method is 1.6 J/mol·K, the lowest among four other methods, followed by those from the method of Ma and Zhao (2.2 J/mol·K) and the method of Myrdal et al. (3.1 J/mol·K). Both Trouton's rule and the method of Kristiakosky (which have average absolute errors of more than 5 J/mol·K) are inadequate for predicting the ΔS_b of hydrogen-bonding compounds. The reason that the proposed method performed so well can be attributed to the use of molecular geometry parameters (σ , τ , ω) and 17 group contribution values. The molecular geometry parameters are unique in that they reflect the ordering of molecules in the liquid that cannot be described by group contribution. The coefficients of 17 group contributors are more reliable than those from the above-mentioned group contribution methods, because they are based on a much larger database (903 compounds in this study, 568 compounds in Hoshino's study, and 483 compounds in Ma and Zhao's study).

VALIDATION OF THE METHOD

To evaluate the strength of the proposed model, the cross-validation was performed.¹² The procedure is as follows: (a) randomize the 903 compounds; (b) remove the first 90 compounds, approximately 1/10 of the total data, to be used as the test set; (c) generate an entropy of boiling equation from the 813 data of the training set; (d) use the newly generated equation to predict the ΔS_b for the test set and calculate the average absolute error for the prediction. Table 4 lists the results of three rounds of cross-validation. The RMSEs for all three different training sets are similar to 2.12 J/mol·K when eq 5 is generated for the whole set 903 compounds. The average absolute errors from each test set are close to 1.5 J/mol·K, the value generated from the 903 compounds, and is close to the one for 31 compounds from the aforementioned method comparison (1.6 J/mol·K).

CONCLUSIONS

The proposed modification of Trouton's rule provides a simple and accurate means of predicting the entropy of

boiling for a large variety of organic compounds. The success is the result of using molecular parameters that reflect both geometric features (σ , τ , ω) and intermolecular association (group contributions).

NOMENCLATURE

ΔS_b = the entropy of boiling
 σ = the rotational symmetry number
 ϕ = the flexibility number
 τ = the effective number of torsional angles
 ω = planarity number
 n_i = occurrence of group i in the compound
 X_i = the contribution of group i to the entropy of boiling
 RMSE = root mean square error
 SE = standard error

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CI990054W