



Estimation of the enthalpy of vaporization of organic components as a function of temperature using a new group contribution method



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ABSTRACT

A new group contribution method has been developed for estimating the enthalpy of vaporization of pure organic compounds as a function of temperature in the range from the standard temperature, 298.15 K, to the normal boiling point. The group contribution parameters have been developed from an experimental database of more than 940 enthalpy of vaporization values. The proposed method is easy to use. The results are discussed and compared with those of currently used models for estimating the enthalpy of vaporization as a function of temperature. This model shows a low average relative error of 1.47% and an average absolute error of 0.55 kJ/mol.

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1. Introduction

The enthalpy of vaporization is one of the most important thermodynamic properties in many chemical processes. The knowledge of this property as a function of temperature is of great importance for the design and operation of multistage vapor–liquid equilibrium and multicomponent processes [1]. The enthalpies of vaporization have also been used to estimate other thermodynamic properties like vapor pressures, molar volumes, Hildebrand's solubility parameters and the Hansen's solubility parameters.

However, it is not always possible to measure or find reliable experimental values of the enthalpy of vaporization as the need arises. In such a situation, accurate and reliable estimation methods play an important role. Therefore, several methods have been reported in the literature to estimate this property. These methods can be divided into several classes such as methods based on ab initio quantum mechanics [2,3], empirical methods [4,5], methods using the Clausius–Clapeyron equation and vapor pressure data [6,7], and methods based on the group contribution approach [8–18]. The first class of methods requires high-level theoretical calculations and significant computing power and their application range is limited especially for the large compounds. The last class of methods, which is widely used, needs mainly tabulated groups (molecular fragments) where it is assumed that the property value of the molecule is a function of the contribution of all the groups and that a property value of any group has the same

contribution in all molecules. The biggest advantage of a group contribution method when compared with other methods, such as quantum mechanics methods, is that it is simple to apply and its applicability to large numbers of compounds.

The method developed in the present work is based on the group contribution approach. This approach has been the subject of an increasing interest and many group contribution methods have been proposed in the recent literature to estimate the enthalpies of vaporization of pure compounds. In general, these methods can be classified in two classes based on the prediction at constant temperatures or as a function of temperature. The first class includes methods for the estimation of enthalpies of vaporization at a constant temperature (e.g., at $T = 298.15$ K, normal boiling point) in which only molecular structure can be used as input parameter. Hukkerikar et al. [8], Gharagheizi et al. [9], Jia et al. [10], Kolská et al. [11], Liu [12] and Joback and Reid [13] proposed some models of this class. However, the temperature dependence of the enthalpy of vaporization was not taken into account in this type of methods. The second class concerns methods for the estimation of enthalpies of vaporization as a function of reduced temperature where the critical temperature is used as input parameter. Among the most important models of this class are those presented by Dalmazzone et al. [14], Basařová and Svoboda [15], Tu and Liu [16] and Xiang [17]. This type of method is more accurate and provides the enthalpies of vaporization at different temperatures.

In this work a new group contribution method has been developed in order to estimate the enthalpy of vaporization of pure organic compounds as a function of temperature in the range from the standard ambient temperature to the normal boiling point. In addition, a new

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fragmentation scheme has been used, based on the work of Cordes and Rarey [19]. This new schema allows to describe a wide variety of organic compounds and to distinguish among isomers. An automatic fragmentation algorithm has been developed using simplified molecular-input line-entry system (SMILES), to eliminate any arbitrary assumptions. The set of molecular fragments is divided into four types of groups: first-order groups, second-order groups, ring corrections and group interactions. The comparison to other group contribution methods is restricted to those that predict the enthalpy of vaporization as a function of temperature and that are applicable over a wide range of components.

2. Experimental data

The first step of this present work is to collect reliable experimental data from the literature. It should be noted that the accuracy of a prediction model depends significantly on the database used for its development. After an extensive evaluation of data, an enthalpy of vaporization database was established for various classes of organic compounds containing hydrocarbons (saturated, unsaturated, cyclic and aromatic), halogenated hydrocarbons, and compounds that contain O, N, and S atoms. The database involves reliable experimental data for 533 organic compounds with more than 940 data points. Most values are given both at the normal boiling point (T_b) and at 298.15 K; others are given in the temperature range from the 298.15 K to T_b , which is the range most often used in the chemical industry. In addition, experimental normal boiling points and critical temperatures are given for each compound.

This experimental database was assembled from several sources [14,20–24]. The molecules are listed according to the increasing number of carbon atoms within each class, but sometimes the carbon number reverts back to lower values because of the inclusion of certain compounds with, secondary or tertiary substitution, multiple functional groups, aromatic substitution, unsaturation, or cyclic structures. More detailed information about the experimental database can be found in the Supplementary material.

3. Proposed group-contribution model

The most general expression of the enthalpy of vaporization as a function of temperature is given by the following equation [14,16,25]:

$$\Delta H_{\text{vap}} = f(T_r)(1 - T_r)^{g(T_r)} \quad (1)$$

where T_r is the reduced temperature (T/T_c) and the function parameters of $f(T_r)$ and $g(T_r)$ are calculated by group contribution techniques from a set of experimental data.

The enthalpy of vaporization decreases with increasing temperature and becomes more pronounced near the critical point with highly non-linear behavior. Based on this finding and our regression analysis, we found the following two-parameters expression to estimate the enthalpy of vaporization of organic compounds:

$$\Delta H_{\text{vap}}(T) = (A - AT_r + AT_r^2)(c_1(1 - T_r))^B \quad (2)$$

where c_1 is an adjustable parameter ($c_1 = 3.261 \times 10^{-3}$); A and B are obtained by summing group contributions: $A = \sum N_i a_i$ and $B = \sum N_i b_i$; N_i is the number of groups of type i ; a_i and b_i are the group contributions of the group i .

As discussed above, the set of groups consists of four types of groups: first-order groups, second-order groups, ring corrections and group interactions. The role of the group interactions is to provide more structural information about polyfunctional compounds with more than one associating functional groups. These group interactions are considered to be non-additive. Steric corrections for branched alkanes were introduced to account for isomer effects and cumulated branching

of methyl groups attached to tertiary or quaternary carbon atoms. Five corrections based on the works of Constantinou and Gani [26] and Domalski and Hearing [27] were introduced: $\text{CH}-(\text{CH}_3)_2$, $\text{C}-(\text{CH}_3)_3$, $\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)$, $\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)_2$ and $\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)_2$. It should be noted that as branching increases for an isomeric hydrocarbon, the ΔH_{vap} value becomes more negative. For example in case of *n*-nonane, the ΔH_{vap} is 46.43 kJ/mol compared to only 38.55 kJ/mol for 2,2,4,4-tetramethylpentane.

The model parameters are estimated using the Levenberg–Marquardt least-squares method. The objective function used in this work is the sum of the squares of the differences between estimated and experimental values of the ΔH_{vap} . The total list of first-order groups, second-order groups, ring corrections and group interactions and their contributions are given in Tables 1, 2, 3 and 4 respectively. General descriptions, sample assignments and occurrences for each group are also supplied.

To illustrate the application of the proposed model, four examples are given in Appendix B for different classes of compounds.

4. Results and discussion

The performance of the proposed model was examined and discussed. An experimental comparison is made with currently-used methods for estimating the ΔH_{vap} as a function of temperature. Three group contribution methods are selected for a comparison of results: second-order group contribution method by Dalmazzone et al. [14] and two first-order group contribution methods by Basařová and Svoboda [15] and Tu and Liu [16]. All of these methods have in common is the fact that they require, in addition to the knowledge of the molecular structure, the critical temperature. Details of these comparisons are reported in the Supplementary material, where for each model the relative errors as well as the average relative errors (ARE) are presented. The most of comparisons were made at the two different temperatures: 298.15 K and the normal boiling point. These comparisons provide valuable information on how well agreement was achieved between experimental and estimated values. The average relative error for each method is defined as follows:

$$\text{ARE}(\%) = \frac{100}{N} \sum_i \left| \frac{\Delta H_{\text{vap}}(\text{exp},i) - \Delta H_{\text{vap}}(\text{pred},i)}{\Delta H_{\text{vap}}(\text{exp},i)} \right| \quad (3)$$

The results show that the proposed method is more accurate than other methods. Table 5 summarizes the average relative errors for all classes of compounds, where the number in superscript indicates the number of compounds included in the comparison. The results achieved by our method are significantly better than those obtained by other methods. While the relative errors are only moderately reduced, as compared to the previous methods, for chlorides, bromides, thiols and sulfides, significant improvements are observed for hydrocarbons (alkanes non-cyclic and cyclic, alkenes non-cyclic and cyclic and aromatics), oxygen compounds (alcohols, ethers, aldehydes, acids, esters, phenols), nitrogen compounds (amines, anilines, pyridines, nitriles), fluorides and mixed halogen compounds.

Table 5 also shows that the two methods formulated by Dalmazzone et al. [14] and Basařová and Svoboda [15] are not applied for all compounds from our database because of a lack of groups required for some classes of compounds or due to numerical errors. The method proposed by Dalmazzone et al. [14] lacks group contribution parameters for some classes of compounds such as polycyclic aromatic compounds, carboxylic acids, fluorides, iodides and mixed halogen compounds (CHClF, CHClBr, CHBrF). Also, due to the reason that the value of the parameter B of Dalmazzone's method [14] can be negative for some compounds (under the square root sign is negative) this method could not be used for the prediction of enthalpy of vaporization (see Supporting information). The method developed by Basařová and Svoboda [15] lacks the contributions of carboxylic acid groups and some multi-ring aromatic groups.

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