



# Prediction of standard enthalpy of formation in the solid state by a third-order group contribution method



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## ABSTRACT

New group contribution model for the prediction of the standard enthalpy of formation in the solid phase of pure compounds is presented. An extensive set of 1222 experimental enthalpies of formation data was collected from different literature sources, evaluated and used to develop this model (85% as the training set and 15% as the test set). The compounds in the data set are composed of hydrogen, carbon, oxygen and nitrogen. The prediction is based exclusively on the molecular structure of the compound and the model results show a good agreement with the experimental data. Compared to the most accurate models for estimating the standard enthalpy of formation in the solid state, this model demonstrates significant improvements in accuracy and applicability.

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## 1. Introduction

One of the most important fundamental thermochemical properties is the standard enthalpy of formation  $\Delta_f H^\circ$ . This property is important for providing thermodynamic information in chemical engineering and materials science [1–6]. It enters into the calculation of energy balances, combustion properties, equilibrium constants of reactions and fuel cell characteristics [7]. Further, the  $\Delta_f H^\circ$  is used in the determination of explosive and propellant properties such as heat of detonation, detonation temperature and detonation pressure [8,9].

The American Institute of Chemical Engineers (AIChE) defines standard enthalpy of formation or standard heat of formation of a compound as the change in enthalpy associated with the reaction forming the given compound in its standard state from the elements in their standard states [10]. The standard state in both cases is the stable phase at 298.15 K and 1 bar.

In chemical industry, particularly in the field of research and development of new energetic materials, having a reliable and accurate method for estimating  $\Delta_f H^\circ$  is absolutely necessary since experimental determination of  $\Delta_f H^\circ$  and synthesis of new

compounds are laborious, costly and even dangerous if the compound concerned is metastable, toxic, or has other hazardous properties.

The great majority of energetic compounds are in the solid state, and determining their  $\Delta_f H^\circ$  values play a key role in several areas such as the design and evaluation of new energy materials [11]. In the literature, there are several methods to estimate the  $\Delta_f H^\circ$  in the gas and liquid states of pure compounds [4,6,12–25] compared to those for estimating the standard enthalpy of formation in the solid state ( $\Delta_f H^\circ_{\text{solid}}$ ) [1,26–29]. This is justified by the fact that the prediction of  $\Delta_f H^\circ_{\text{solid}}$  of organic molecules at solid state from their molecular structures is a difficult task by the effects of molecular packing and polymorphism in some solid compounds [11]. Indeed, the prediction of thermodynamic properties of organic compounds in the solid-state needs a good knowledge of the most stable or most likely molecular structure.

The Methods for determining the  $\Delta_f H^\circ_{\text{solid}}$  values of pure components can roughly be divided into two important classes: quantum mechanical approach [19,30–32] and group contribution approach [1,13,26–29]. Quantum mechanical methods provide generally reliable predictions for very small molecules [12]. However, these methods require high-level theoretical calculations and significant computing power. By using quantum mechanical approach, several authors viz. Keshavarz et al. [33], Kim et al. [31], Mathieu and Simonetti [19], Rice et al. [30] and Politzer et al. [32]

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|-----------------------------------|--|
| $\Delta_f H^\circ$                | standard enthalpy of formation (kJ/mol)                    |
| $\Delta_f H^\circ_{\text{solid}}$ | standard enthalpy of formation in the solid state (kJ/mol) |
| AD <sub>max</sub>                 | absolute maximum deviation (kJ/mol)                        |
| AAD                               | average absolute deviation (kJ/mol)                        |
| SD                                | standard deviation (kJ/mol)                                |
| R <sup>2</sup>                    | coefficient of determination                               |

proposed to estimate  $\Delta_f H^\circ_{\text{solid}}$  from the difference between the calculated gas phase formation enthalpies and sublimation enthalpies. Their methods showed a low deviation from experimental data only for a small data set of organic compounds. They estimated enthalpies of formation in the gas phase by using different density functional theory methods. For computation of sublimation enthalpies, Keshavarz et al. [33] and Rice et al. [30] have used the molecular surface area, total average potentials and the positive and negative variance of the surface electrostatic potential. As for other authors they modified the van der Waals electrostatic surface potentials of individual molecules for computation of the sublimation enthalpy.

The group contribution method, which is popular, is one of the most widely used methods applied to predict thermodynamic properties of organic compounds [12,14,34–38]. Group contribution methods are inexpensive to apply and necessitate only tabulated group contribution values. Fewer group contribution models, however, have been proposed for the prediction of  $\Delta_f H^\circ_{\text{solid}}$  in the solid state. Domalski and Hearing [29] and Cohen [28] showed that the estimation of  $\Delta_f H^\circ_{\text{solid}}$  of organic compounds can be carried out in a satisfactory manner using the Benson's method [17] which is a second-order group contribution method primarily developed so as to estimate different thermodynamic properties in the gas phase. Domalski and Hearing [29] have used a limited list of 57 C–H, 140 C–H–O, and 147 C–H–N–O compounds to develop a model for estimating  $\Delta_f H^\circ_{\text{solid}}$ . In the three phases, values of their model showed that 67% of deviations were  $< \pm 4$  kJ/mol, 16% of deviations were  $> \pm 4$  kJ/mol but  $< \pm 8$  kJ/mol, and 17% were  $> \pm 8$  kJ/mol. The model proposed by Cohen [28] allows the estimation of  $\Delta_f H^\circ_{\text{solid}}$  only for C–H and C–H–O compounds with a limited range of applicability. His model demonstrated good estimation ability as evidenced by mean deviations from the 538 compounds of 9.1 kJ/mol. Recently, Salmon and Dalmazzone [26] used a second-order group contribution method to estimate  $\Delta_f H^\circ_{\text{solid}}$  of large data set of 1017 organic compounds in the solid state (145 C–H, 256 C–H–O, 482 C–H–N and C–H–N–O compounds). They proposed a significant number (480) of groups and corrections viz. 365 groups, 81 ring strain corrections and 34 non-nearest neighbour interactions. Among these 480 groups and corrections, 39.37% (189) of them are generated by only one compound. Their model showed an average absolute deviation, standard deviation, maximum and minimum deviations of 22.26 kJ/mol, 52.1 kJ/mol, 393.9 kJ/mol and  $-389.7$  kJ/mol, respectively. More recently, Keshavarz [1,39,40] has proposed several simple correlations to estimate  $\Delta_f H^\circ_{\text{solid}}$  for some classes of energetic compounds using the contribution of some simple polar groups and specific molecular fragments. The author has employed limited lists of energetic compounds in his works viz. 192 C–H–N–O energetic compounds [1], 29 of nitro-aromatic compounds [39] and 78 C–H–N–O nitro-compounds [40]. The average absolute deviations of these three correlations compared with experimental data are 27.8, 10.6 and 42.3 kJ/mol, respectively. A thorough comparison between the previous group contribution methods for predicting  $\Delta_f H^\circ_{\text{solid}}$  reveals that the Salmon and Dalmazzone method [26] is more accurate than previous methods.

In this paper, we present a new group contribution model to predict  $\Delta_f H^\circ_{\text{solid}}$  of organic compounds containing carbon, hydrogen, oxygen and nitrogen atoms. In the literature, there are many fragmentation schemes which are used to develop a group contribution method. One of the better group contribution schemes was developed by Marrero and Gani [41] for estimating physical and thermodynamic properties with a wide range of applicability to deal with small, large, multifunctional and complex compounds. In this work, we used Marrero–Gani's scheme to provide the structural groups. This scheme can provide a set of molecular fragments (groups) that can capture all significant effects on the property to be predicted thus allowing to describe a wide variety of organic compounds while distinguishing among isomers [12,14,41]. The Marrero–Gani's groups are divided into three types of groups: first-order, second-order and third-order groups. The first-order groups are composed of a large set of simple groups that allow describing a wide variety of organic compounds. However, these groups capture incompletely the proximity effects and differences among isomers. For this reason, Marrero and Gani [41] have introduced second level groups. Although these second-order groups significantly improve the description of the molecular structure of some classes of compounds, they are unable to describe aromatic or cycloaliphatic compounds with multi-ring and complex heterocyclic, and large poly-functional acyclic compounds. To account for these classes of compounds and to refine the accuracy of the estimated values, Marrero and Gani [41] have introduced the third-order groups. For the determination of group contribution parameters, Marrero and Gani propose to use three consecutive steps. In the first step, only the first-order groups are considered. However, in the second step the regression is realised using first-order and second-order groups, but the parameters of first-order groups are kept fixed. In the step 3, both the contributions of first-order and second-order groups are kept fixed to determine the contributions of the third-order groups.

The objective of this work is to develop a simple accurate model for the prediction of  $\Delta_f H^\circ_{\text{solid}}$  at solid state from the molecular structures of pure compounds with a wide range of applicability, and to show a detailed analysis of its performance compared to previous models. The Marrero and Gani scheme is used. To improve the reliability and accuracy of proposed model, especially in the case of C–H–N and C–H–N–O compounds, new structural groups are defined and included in the Marrero and Gani scheme based on the analysis of the predicted results and molecular structure compounds.

## 2. Experimental data

The experimental values of  $\Delta_f H^\circ_{\text{solid}}$  presented by National Institute of Standards and Technology (NIST) [42] were collected and implemented with those recently published [26,27,33,43,44] to provide the reliable data set. The data set used in the present study is comprised of 1222 experimental data points including 170 C–H, 341 C–H–O, 158 C–H–N and 553 C–H–N–O compounds. All values stored in the data set, ranging in molecular masses from 59.06 up to 942.97 g/mol, are derived from experimental data and range in  $\Delta_f H^\circ_{\text{solid}}$  values from  $-2624$  up to 1218.6 kJ/mol. The  $\Delta_f H^\circ_{\text{solid}}$  values are expressed in kJ/mol which facilitated the comparison of proposed model results with those of other research. The use of kJ/kg is also possible, but it can lead to inaccurate and wrong conclusions during the validation of the model since larger molecules tend to have smaller value than higher molecules.

In the literature, a simple review of experimental  $\Delta_f H^\circ_{\text{solid}}$  values will reveal some large discrepancies in reported enthalpies of formation. Some examples can illustrate this fact: 2,4,6-trinitrotoluene, cyclotetramethylenetetra-*trans*-nitramine, phenanthrene, oxamide, resorcinol, biphenyl, pyrene,

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