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PII: S0378-3812(13)00321-X
DOI: http://dx.doi.org/doi:10.1016/j.fluid.2013.06.046
Reference: FLUID 9636

To appear in: *Fluid Phase Equilibria*

Received date: 26-3-2013
Revised date: 18-6-2013
Accepted date: 21-6-2013

Please cite this article as: F. Gharagheizi, P. Ilani-Kashkouli, W.E. Acree Jr., A.H. Mohammadi, D. Ramjugernath, A Group Contribution Model for Determining the Sublimation Enthalpy of Organic Compounds at the Standard Reference Temperature of 298 K, *Fluid Phase Equilibria* (2013), http://dx.doi.org/10.1016/j.fluid.2013.06.046

A Group Contribution Model for Determining the Sublimation Enthalpy of Organic Compounds at the Standard Reference Temperature of 298 K

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Abstract — The sublimation enthalpy provides a measure of molecular interactions in the solid phase. Practical applications involving sublimation enthalpies include the estimation of the crystal lattice energy of molecular crystals, estimation of the enthalpy of solvation of crystalline organic compounds, and prediction of the environmental fate and vapor pressures of solid compounds. Recently an extensive compilation of phase change enthalpies, including sublimation enthalpies of pure organic and organometallic compounds, was published [1]. This collection of sublimation enthalpies for 1269 compounds at the standard temperature of 298.15 K was used in this study for the development of a predictive model. The compounds in the collection are composed of carbon, hydrogen, nitrogen, oxygen, phosphorous, sulfur, fluorine, chlorine, bromine, and iodine. This paper presents a reliable group contribution model for the estimation of the sublimation enthalpies of organic compounds. The group contribution model developed is able to predict the standard molar enthalpies of sublimation to within an average absolute relative deviation of 6.4%, which is of sufficient accuracy for many practical applications.

Keywords: Sublimation enthalpy, Group Contribution, Organic Compounds; Chemical Structure, Reliable model.

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1. Introduction

The enthalpy change associated with a change in phase is of great importance in various disciplines such as chemical and environmental engineering, chemistry, and physics due to the fact that it provides a measure of intra- and intermolecular interactions [1].

As one of the phase change enthalpies, the sublimation enthalpy is considered as a measure of intermolecular forces of substances in the solid phase [2]. The crystal lattice energy which is the energy that constitutes a crystal from the isolated gas phase molecules is directly calculated from the sublimation enthalpy. Therefore, this parameter is used to determine the specific packing of solid state crystalline substances [3]. As a consequence of such capability, sublimation enthalpy is used to describe the solvation of molecules, particularly drug molecules [4-9].

The sublimation enthalpy is also used to evaluate the transport of contaminants in the atmosphere; in environmental fate modeling; to determine discoloration of materials; and determine dispersion of dyes [10]. Furthermore, it can be used to calculate the standard molar enthalpy of formation of crystalline compounds in the gas phase from measured enthalpy of combustion data. Moreover, it can be used to estimate other physical properties such as vapor pressure through the well know Clausius-Clapeyron equation [11].

Several methods have so far been proposed for the estimation of sublimation enthalpies of pure compounds at standard temperature, viz. 298.15 K. Rice et al. [12] used the properties associated with quantum mechanically determined electrostatic potentials of isolated molecules to correlate the sublimation enthalpies of a dataset of 35 pure organic compounds. The root mean

square error (*RMSE*) and the maximum deviation of the model from experimental data were reported as 15 and 52 kJ.mole^{-1}, respectively. Several other proposed models, viz. Politzer et al. [13], Matheieu and Simonetti [14], and Kim et al. [15] independently modified the van der Waals electrostatic surface potentials. Implementing these modifications, they developed several parameters to calculate the sublimation enthalpy. Their models showed low deviation from experimental data for a small dataset of 34 organic compounds. In another proposed model, Ouvrard and Mitchell [16] used the number of occurrences of various atom types as descriptors to correlate the sublimation enthalpy. The authors employed a training set comprised of 226 compound for developing the basic model and another dataset of 35 compounds as a test set for assessing the model's predictive capability for which they reported squared correlation coefficients (R^2) of 0.925 and 0.937, respectively. Politzer et al. [17] suggested a three-term expression for correlating the sublimation enthalpies that employed as input parameters the molecular surface area and information based on surface electrostatic potential. The input parameters were computed at the B3PW91/6-31G** level. The correlation model derived predicted the sublimation enthalpies of 105 amino acids and small organic compounds to within an average absolute deviation of 11.7 kJ mol^{-1}. Byrd and Rice [18] used quantum mechanical data to predict the sublimation enthalpy. They stated that their model can estimate the sublimation enthalpies of 35 organic compounds with a *RMSE* and maximum deviation of 12.5 and 217.7 kJ.mole^{-1}, respectively.

To date, a few models have been proposed for the estimation of sublimation enthalpy at the triple point. As a first attempt, Gaharagheizi [19] proposed a 5-parameter quantitative structure property relationship (QSPR) for the estimation of the sublimation enthalpies of 1348 pure chemical compounds. The R^2, RMSE, and maximum absolute relative deviation of the

model from DIPPR 801 data were 0.9746, 5.46, and 27.56 kJ.mole^{-1}, respectively. In a follow-up study, Gharagheizi et al. [20] used an artificial neural network-group contribution approach to correlate the sublimation enthalpies of 1384 pure chemical compounds. The model demonstrated good descriptive ability as evidenced by the R^2, average absolute relative deviation (*AARD%*), and root-mean square error of 0.986, 3.54% and 4.21 kJ.mole^{-1}, respectively.

Mathieu [21] used a subset of the dataset used by Gharagheizi [19] (1300 out of 1348 data) to develop a 31 parameter-model based on the fragment contributions. The R^2, *RMSE*, and *AARD%* of the model compared with DIPPR 801 are 0.986, 4 kJ.mole^{-1}, and 3.1%, respectively. More recently, Salahinejd et al. [22] employed another subset of the dataset used by Gharagheizi [19] (1304 out of 1348 data) to obtain a 4 parameter-QSPR model for the prediction of the sublimation enthalpy. The authors reported values of 0.96 and 7.9 kJ.mole^{-1} for the R^2 and the average absolute error of their model, respectively. The results show that the latter model predicts the sublimation enthalpy with a lower accuracy than the one proposed by Gharagheizi [19]. Neither Mathieu [21], nor Salahinejd et al. [22] mentioned why they eliminated 48 and 44 compounds, respectively, from the complete dataset implemented by Gharagheizi [20].

A thorough comparison among the previous models proposed for the estimation of the sublimation enthalpy of pure chemical compounds reveals that:

1- Most of the previous models for the estimation the sublimation enthalpy at the standard temperature of 298.15 K have been developed/evaluated for small chemical groups/families of compounds. Furthermore, the largest data set was used by Ouvrard [16] (261 compounds).

2- Among the various models for the estimation of the sublimation enthalpy at the triple point, the model proposed by Gharagheizi et al. [20] shows better results and is more comprehensive that the others.

Recently, Acree and Chickos [1] reviewed the literature for published phase change enthalpies at the standard temperature of 298.15 K over the period of 1880-2010 and presented their results as a massive compilation. The main aim of this study is to develop a group contribution method using the data compilation, along with published enthalpy of sublimation [23-119] data over the past three years.

2. Experimental enthalpy of sublimation database

As mentioned earlier, the data compilation presented by Acree and Chickos [1] together with recently published data over the past three years [23-119] was implemented to provide the dataset of sublimation enthalpies of compounds used in this study. The enthalpies of sublimation were determined by well-established experimental methodologies, including "vacuum sublimation" drop microcalorimetry, Knudsen mass-loss effusion, transpiration, and correlation gas chromatography combined with differential scanning calorimetric measurement of the enthalpy of fusion. Correlation gas chromatographic measurements which pertain to enthalpies of vaporization, $\Delta_{vaporization}H_m^o$, and the enthalpy of fusion, $\Delta_{fusion}H_m^o$, are needed to convert the measured $\Delta_{vaporization}H_m^o$ to $\Delta_{sublimation}H_m^o$, e.g., $\Delta_{sublimation}H_m^o$ (T = 298.15 K) = $\Delta_{vaporization}H_m^o$ (T = 298.15 K) + $\Delta_{fusion}H_m^o$ (T = 298.15 K). For many of the compounds the measurements were performed at mean temperatures, T_{mean}, higher than 298.15 K, in which case the measured

enthalpy of sublimation was corrected back to 298.15 K using the standard thermodynamic relationship

$$\Delta_{sub\,\mathrm{lim}\,ation} H_m{}^o(T = 298.15) = \Delta_{sub\,\mathrm{lim}\,ation} H_m{}^o(T = T_{mean}) + \Delta C_p{}^o(298.15 - T_{mean}) \quad (1)$$

where ΔC_p^o is the molar heat capacity difference between the crystalline and gaseous forms of the organic compound. Researchers reporting $\Delta_{sublimation}H_m^o$ data have estimated the required ΔC_p^o values in different ways. Some used a generic value of -8.314 J mol^{-1} K^{-1} [120], while others used group contribution methods [121], or measured heat capacity data for the crystalline compound combined with estimated gas phase heat capacities from statistical thermodynamics using the vibrational frequencies from quantum mechanical B3LYP/6–31G(d) calculations [122]. We have used the enthalpies of sublimation as reported by the authors as there was often insufficient experimental data given in the published papers for us to make corrections in a consistent manner. Some papers simply gave the the enthalpy of sublimation corrected to 298 K with no additional information. The reported experimental uncertainty given by the reporting authors rarely included the uncertainty associated with extrapolating the measured values to 298.15 K.

Roux et al. [123] compiled and critically evaluated published thermodynamic data for polycyclic aromatic hydrocarbons (PAHs). As part of their evaluations the authors did recommend numerical values for $\Delta_{sublimation}H_m^o$ (T = 298.15 K) for the compounds they studied. Our database includes includes many of (though not all of) the PAH compounds considered by Roux et al. We considered only those compounds where the reporting authors had given a $\Delta_{sublimation}H_m^o$ (T = 298.15 K) value. For most of the PAH compounds common to both databases, the average values that we have used in developing our group contribution method

were within 1 to 2 kJ.mol^{-1} of the recommended values of Roux et al. [123]. The notable exceptions were for chrysene, dibenz[a,c]anthracene, dibenz[a,h]anthracene, naphthacene, and pentacene where we have elected to use the $\Delta_{sublimation}H_m^o$ (T = 298.15 K) values given by the reporting author [124]. Roux et al. [123] stated that they believed the correction used to extrapolate the measured $\Delta_{sublimation}H_m$ (T = T_{mean}) back to 298 K was too large, and they used a different set of ΔC_p^o values.

The database used in the present study is comprised of 1645 experimental data points for 1269 compounds. A single experimental value was reported for 1018 compounds. Multiple values were reported for 251 of the 1269 compounds, in which case the arithmetic averages were used. No attempt was made to select between the independently determined values, which for the most part differed by less than 6 kJ mol^{-1}. Several of the more notable exceptions to this were: 2-imadazolinone where the observed enthalpy of sublimation ranged from 83.7 kJ to 96.6 kJ mol^{-1}; 3,4-dihydroxy-3-cyclobutene-1,2-dione where the enthalpy of sublimation ranged from 83.7 kJ mol^{-1} to 154.3 kJ mol^{-1}; cytosine where the enthalpy of sublimation ranged from 155 to 176 kJ mol^{-1}; tetrahydro-2-pyrimidone where the enthalpy of sublimation ranged from 89.3 kJ to 113.4 kJ mol^{-1}; 1,3-dithiane where the enthalpy of sublimation ranged from 52.3 to 69.9 kJ mol-1; 4-hydroxypyridine where the enthalpy of sublimation ranged from 103.8 to 118.6 kJ mol^{-1}; 5-methyluracil from 131.3 to 138 kJ mol^{-1}; 3-pyridinecarboxylic acid where the enthalpy of sublimation ranged from 105.2 to 123.9 kJ mol^{-1}; 1,2,3-trihydroxybenzene where the enthalpy of sublimation ranged from 104 to 116.9 kJ mol^{-1}; hexanamide where the enthalpy of sublimation ranged from 85 to 98.7 kJ mol^{-1}; 2-brombenzoic acid where the enthalpy of sublimation ranged from 95.9 to 108.5 kJ mol^{-1}; 2-iodobenzoic acid where the enthalpy of sublimation ranged from 92.6 to 112.8 kJ mol^{-1}; 2-iodobenzoic acid where the enthalpy of sublimation ranged from 96.4

to 111.1 kJ mol^{-1}; 4-iodobenzoic acid where the enthalpy of sublimation ranged from 99.3 to 112.9 kJ mol^{-1}; 2,4,6-trinitrotoluene where the enthalpy of sublimation ranged from 104.6 to 113.2 kJ mol^{-1}; benzimidazole where the enthalpy of sublimation ranged from 94.3 to 102.2 kJ $mole^{-1}$; 3-hydroxybenzoic acid where the enthalpy of sublimation ranged from 118.3 to 125 kJ mol^{-1}; 4-hydroxybenzamide where the enthalpy of sublimation ranged from 117.8 to 129.7 kJ mol^{-1}; 1,3-dimethylxanthine where the enthalpy of sublimation ranged from 135 to 144 kJ mol-1; (2,4-dichlorophenoxy)acetic acid where the enthalpy of sublimation ranged from 115 to 125 kJ mol^{-1}; for coumarin where the enthalpy of sublimation ranged from 83.1 to 95.4 kJ mol^{-1}; 2-(2,4-dichlorophenoxy)propanoic acid where the enthalpy of sublimation ranged from 116 to 130 kJ mol^{-1}; for 2,4,6-trimethylphenol where the enthalpy of sublimation ranged from 82.8 to 95 kJ mol^{-1}; 2-adamantone where the enthalpy of sublimation ranged from 66.3 to 80.3 kJ mol^{-1}; and tetraphenylmethane where the enthalpy of sublimation ranged from 140 to 150.6 kJ mol^{-1}. In total a collection of standard molar enthalpies of sublimation was obtained for 1270 unique pure chemical compounds at 298.15 K.

A careful analysis of the compounds within the dataset shows that the sublimation enthalpies range between 34 and 240 kJ.$mole^{-1}$. The compounds are composed of carbon (1 to 34 atoms per compound), hydrogen (1 to 48 atoms per compound), nitrogen (1 to 7 atoms per compound), oxygen (from 1 to 14 atoms per compound), phosphorus (only 1 atom per compound), sulfur (1 to 6 atoms per compound), fluorine (1 to 34 atoms per compound), chlorine (1 to 6 atoms per compound), bromine (1 to 4 atoms per compound), and iodine (1 to 2 atoms per compound) atoms. There are 117 hydrocarbons (C and H compounds) in the dataset whose sublimation enthalpies range from 37 to 182 kJ.$mole^{-1}$. The dataset includes 113 nitrogen compounds whose sublimation enthalpies range from 34 to 199 kJ.$mole^{-1}$. The elemental

composition analysis of the dataset further shows that there are 918 oxygen compounds whose sublimation enthalpies range from 45 to 239 kJ.mole^{-1}. There are 112 sulfur compounds in the dataset having sublimation enthalpies that range from 54 to184 kJ.mole^{-1}. There are a significant number of halogen compounds within the dataset: 55 fluorine-containing compounds with sublimation enthalpies between 62 and 134 kJ mol^{-1}; 116 chlorine-containing compounds with sublimation enthalpies between 60 and 183 kJ mol^{-1}; 33 bromine-containing compounds having sublimation enthalpies that range from 54 to 152 kJ.mole^{-1}; and 16 iodine-containing compounds whose sublimation enthalpies range from 70 to 127 kJ.mole^{-1}. The number of phosphorous compounds in the dataset is much smaller (5 compounds) and their sublimation enthalpies range from 75 to 143 kJ.mole^{-1}. The chemical diversity of the dataset considered in the present study is significantly greater than datasets used in earlier studies [13-23] involving the prediction of sublimation enthalpies.

In order to obtain a predictive model, the data set was split into three sub-data sets; the first set for developing the model (called the "training set"), the second set for assessing the internal validity of the model (called the "validation set"), and the final set for evaluating the predictive capability of the derived model (called the "test set"). The division of the data can be performed randomly; however, this may lead to an inappropriate allocation of compounds to each sub-dataset; in other words all of the larger enthalpies of sublimation might end up in the test set. In order to avoid this potential problem, one can use the *K*-means clustering technique [125, 126]. This method partitions a dataset into *n* sub-datasets in which each data point belongs to the subset with the closest mean. This procedure resolves the issue of inappropriate allocation of datasets. Another point is the quota of each sub-dataset from the main dataset. It has been shown that if training set is too small, the produced model doesn't have predictive power.

Moreover, if the dataset is too large, the model may produce significantly better results for the training set rather than for the validation and test sets [127]. In order to prevent these issues, nearly 80% of the data set was allocated to the training set (1015 data points) and the remaining data points were allocated evenly between the respective validation and test sets (127 data points each).

3. Model development

To develop a reliable correlation model, one must use parameters which enable one to distinguish each compound from the others. In other words, one needs a unique set of parameters for each compound that can adequately describe the sublimation enthalpy. Based on past experience [20, 21] it was decided to generate the parameters from the molecular structures. As a result, a collection of 294 chemical substructures were gathered which have previously been implemented by the authors to correlate other important physical properties [20, 128-131]. In the next step, the frequency of appearance of each of these 294 chemical substructures was counted in each compound. The pair correlation between each pair of the 294 chemical substructures was then evaluated to avoid entering irrelevant parameters into the final model. In the next step, if the pair correlation of a pair of chemical substructures was more than the threshold value of 0.95, one of them was eliminated and the other kept for the next step. Performing this procedure, the collection of the chemical substructures was reduced to 251 chemical substructures. In order to determine the final model and to choose the optimal subset of chemical substructures affecting the sublimation enthalpy, the sequential search method was applied [129]. The major target of a sequential search is to find an optimal subset of chemical substructures for a specified model

size. The basic idea of the method is to replace each chemical substructure, one at a time, with all the remaining ones and see whether a better model is obtained.

To accomplish this, both R^2 and *AARD%* were used to evaluate the improvement by adding a new chemical substructure to the model. The statistical parameters used in this article are defined in Appendix A.

4. Result and discussion

In order to obtain a reliable model, the collection of 251 chemical substructures prepared in the previous step, was introduced to the sequential search algorithm.

The gradual changes in R^2 and *AARD%* as a function of an incremental increase in the number of chemical substructures is depicted in Figure 1.

Figure 1

In order to find the optimal model in terms of both the number of chemical substructures and accuracy, a threshold value of 0.01 was considered for the decrease in *AARD%* as a stopping criterion. It means that when the improvement of the model *AARD%* was less than 0.01, the sequential search algorithm was automatically stopped and reported the final model. The optimal model was obtained using 147 chemical substructures. This point is depicted as a green pentagram sign in Figure 1. The model obtained is as follows:

(2)

$$\Delta_{sublimation}H_m(kJ.mol^{-1}) = \sum_{i=1}^{147} n_i \times \Delta_{sublimation}H_m{}^{i} + \Delta_{sublimation}H_m{}^{0}$$

where $\Delta_{sublimation}H_m{}^{0}$, $\Delta_{sublimation}H_m{}^{i}$ and n_i are the intercept of the equation, the contribution of the *i*th chemical substructure to the sublimation enthalpy, and the number of occurrences of the *i*th chemical substructure in every chemical structure of pure compounds, respectively. The subset of 147 chemical substructures and their contribution to the sublimation enthalpy are tabulated in Table 1.

Table 1

The predicted sublimation enthalpies and their absolute relative deviation from the experimental values are presented as a supplementary table.

The model results show that it can successfully predict the standard molar enthalpies of sublimation of pure organic compounds at 298 K. The average absolute relative deviation, standard deviation error, and root mean square error of the model are 6.3%, 10.5, and,10.5 for the training set; 6.3%, 10.7, and 10.7 for the validation set; and 6.3%, 12.7, and 10.8 for the test set, respectively. The values are based on the model predictions and their corresponding experimental values.

For graphical presentation of the applicability domain of the model and the outliers, the Williams [132] plot is depicted in Figure 2.

Figure 2

This plot shows the correlation of hat values and standardized residuals. It should be noted that the hat values and standardized residuals values are presented in a supplementary table for all the compounds. A warning leverage (h*=0.35) - blue vertical line – is generally fixed at 3n/p, where n is number of training chemicals and p the number of model variables plus one. The leverage of 3 is considered as a cut-off value to accept the points that lie ± 3 (two horizontal red lines) standard deviations from the mean (to cover 99% normally distributed data). The applicability domain is located in the region of $0 \leq h \leq 0.35$ and $-3 \leq R \leq +3$. Existence of the majority of data points in this domain shows that both model development and prediction are performed within the applicability domain which results in a valid model. The points depicted with red circles (3<R or R<-3) are "bad high leverage" points and represent outliers of the model. This erroneous prediction could probably be attributed to incorrect experimental data rather than to the molecular structure [132]. These points are highlighted in the supplementary table.

According to the results, the model can predict the sublimation enthalpies of 117 hydrocarbons with an *AARD%* of 6.7%. There are 24 hydrocarbons for which the model shows a deviation of more than 10%. A careful consideration of the hydrocarbons demonstrates that they are multi-ring complicated compounds. The chemical structures of these 24 hydrocarbons are shown in Table 2. We do note that chrysene, dibenz[a,c]anthracene, dibenz[a,h]anthracene, naphthacene, and pentacene are among the 24 hydrocarbons showing the larger deviations. Our predicted values of 114.4 $kJ.mol^{-1}$ (123.4 $kJ\ mol^{-1}$) for chrysene, of 148.9 $kJ.mol^{-1}$ (135.4 $kJ.mol^{-1}$) for diben[a,h]anthracene, 129.9 $kJ.mol^{-1}$ (145.9 $kJ.mol^{-1}$) for dibenz[a,c]anthracene, 116.3 $kJ.mol^{-1}$ (135.9 $kJ.mol^{-1}$) for naphthacene, and 137.3 $kJ.mol^{-1}$ (165.5 $kJ.mol^{-1}$) for pentacene are in better agreement with the recommended values of Roux et al. (which are given in parentheses)

than the reported $\Delta_{sublimation}H_m^o$ (T = 298.15 K) values of DeKruif [124]. Figure 3 depicts the predicted sublimation enthalpies of hydrocarbons versus the corresponding experimental values.

Figure 3

Table 2

The model predictions for nitrogen compounds versus. the corresponding experimental sublimation enthalpies are presented in Figure 4. As demonstrated, the *AARD%* of the model from experimental data is 6.8%. According to the Williams plot depicted in Figure 2, many outliers of the model are for nitrogen compounds. This may be the major cause of high deviation in the prediction of the sublimation enthalpy for these nitrogen compounds.

Figure 4

The *AARD%* of the model results from experimental sublimation enthalpy for oxygen compounds is 6.2%. The predicted values versus the corresponding experimental data are shown in Figure 5. Like nitrogen compounds, the majority of highly deviating oxygen compounds are outliers. Therefore, their experimental data may be erroneous.

Figure 5

There are just 5 phosphorous compounds within the data set for which the model gives a promising *AARD%* of 0.1%.

Sulfur compounds are another class of compounds for which the model shows an *AARD%* of 4.7%. There are 18 compounds for which the model gives an *ARD%* of higher than 10%. The

compounds are presented in Table 3. The predicted versus experimental sublimation are shown in Figure 6.

Table 3

Figure 6

Fluorine compounds are one of the important classes of compounds whose sublimation enthalpies are predicted by the model with an *AARD%* of 5.9%. Their predicted versus experimental sublimation data are shown in Figure 7.

Figure 7

The model predicts the sublimation enthalpies of chlorine compounds better than fluorine compounds in terms of AARD% (5% vs. 5.9%). Their predicted versus experimental sublimation data are shown in Figure 8.

Figure 8

Based on the model analysis, the sublimation enthalpies of bromine compounds are successfully predicted by the model. The model AARD% for this class of compounds is 3.1% which is less than those of halogen compounds mentioned above. Figure 9 depicts the predicted sublimation enthalpies of bromine compounds versus their corresponding experimental values.

Figure 9

Iodine compounds are another class of halogen compounds whose sublimation enthalpies are successfully predicted by the model. The model shows a low *AARD%* of 2.6% which is the minimum deviation among all the lighter halogen compounds that have been studied. Figure 10 depicts the predicted sublimation enthalpies of iodine compounds versus their corresponding experimental values.

Figure 10

The AARD% of the model from experimental sublimation enthalpies of various classes of compounds are shown in Table 4.

Table 4

Unfortunately, a comprehensive comparison between the presented model and the previous models is not possible because they have mostly developed for small groups/classes of compounds. Even the largest dataset used by Ouvrard and Mitchell [16] which comprised of sublimation enthalpies of 261 organic compounds, when compared with the data used in this study is very small.

In order to compare the performance of the presented model developed in this study with that proposed by Ouvrard and Mitchell [16], a comparison was made based on the chemical families of compounds that were used by Ouvrard and Mitchell [16] in their studies. They categorized the compounds within their data set as aliphatic hydrocarbons, aromatic hydrocarbons, and non-hydrogen bonding compounds. We used the same classification for our main dataset in order to make a comparison. The results are presented in Table 5. As can be seen, the model presented by Ouvrard and Mitchell [16] predicts the sublimation enthalpies of the

aliphatic and aromatic hydrocarbons slightly better than the model presented in our study. A similar behavior can be observed for non- hydrogen bonding compounds. It should be noted that the number of hydrocarbons in our dataset is significantly larger than that of Ouvrard and Mitchell [16]. Another point to consider is that majority of the compounds for which the experimental sublimation enthalpies have been reported are capable of forming hydrogen bonding. However, most of the compounds used by Ouvrard and Mitchell [16] to develop their model are non-hydrogen bonding. This latter detail may be considered as a drawback of thir model.

Table 5

4. Conclusions

A group contribution model was developed for the prediction of the standard molar enthalpies of sublimation at 298.15 K, $\Delta_{sublimation}H_m^o$ (T = 298.15 K), for organic compounds. The validity and the predictive capability of the model were assessed using a validation set and a test set, respectively. The model is capable of predicting $\Delta_{sublimation}H_m^o$ (T = 298.15 K) values of organic compounds with an acceptable average absolute relative deviation between predicted and experimental values of 6.4%. The dataset used in this study is comprised of 1269 organic compounds containing carbon, hydrogen, nitrogen, oxygen, phosphorous, sulfur, fluorine, chlorine, bromine and iodine atoms. Analysis of the model shows that the model can estimate the sublimation enthalpies of hydrocarbons, and compounds containing nitrogen, oxygen,

phosphorous, sulfur, fluorine, chlorine, bromine and iodine atoms to within acceptable average relative deviations of 6.9%, 6.8%, 6.2%, 0.1%, 5.7%, 5.9%, 5%, 3.1% and 2.6% from the corresponding experimental values, respectively. The parameters needed to predict the sublimation enthalpies are the number of occurrences of 147 simple chemical substructures in the compound under consideration and the numerical values of each substructure contribution to $\Delta_{sublimation}H_m^o$ (T = 298.15 K) given in Table 1.

Acknowledgements

This work is based upon research supported by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation.

Appendix A

The mathematical definition of the relative deviation (RD%), average absolute relative deviation (AARD%), root mean square error (RMSE), standard deviation error (Std), and squared correlation coefficient (R^2) are presented as follows:

(A1)

$$RD\% = 100 \times \frac{pred - lit}{lit} \tag{A2}$$

$$AARD\% = \frac{100}{N}\sum_{i}^{N}\frac{|\ pred(i) - lit(i)\ |}{lit(i)} \tag{A3}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(pred(i) - lit(i))^2}{N}} \tag{A4}$$

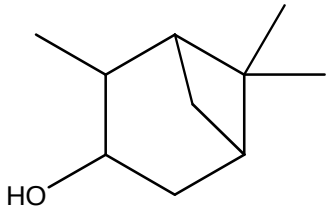
$$Std = \frac{1}{\mathrm{N}}\sum_{i}^{\mathrm{N}}\sqrt{\left(\mathrm{pred(i)} - \overline{\mathrm{pred}}\right)^2} \tag{A5}$$

$$R^2 = 1 - \frac{\sum_{i}^{N}(pred(i) - lit(i))^2}{\sum_{i}^{N}(pred(i) - \overline{lit})^2}$$

where *pred* and *lit* denote the predicted value by model and its corresponding value reported by literature, respectively. The terms $\overline{\mathrm{pred}}$ and $\overline{lit}$ refer to the mean values over the predicted values by the model and the mean value over the literature reported data. *N* is the number of data point in each data set or subset.

Appendix B

Example 1:
(1R,2R,3R,5S)-(-)-isopinocamheol



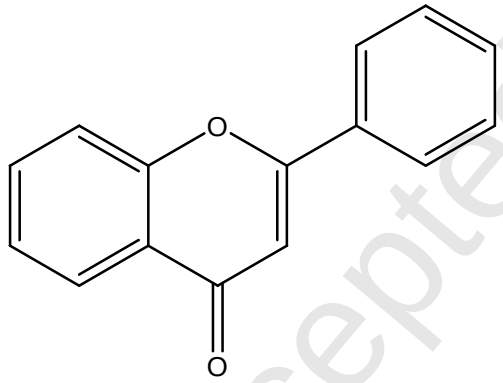
Experimental value: 80.5±1.1 kJ.mole^{-1}

Predicted value: 82.74 kJ.mole^{-1} (2.8% deviation)

ID	$\Delta_{Sublimation}H_m^i$	Number	Value	Number x VALUE
	$\Delta_{sublimation}H_m^0$		17.22158	17.22157658
1	$\Delta_{sublimation}H_m^1$	3	1.839585	5.518755471
2	$\Delta_{sublimation}H_m^2$	3	4.324475	12.97342471
3	$\Delta_{sublimation}H_m^3$	3	-3.17657	-9.529707593
4	$\Delta_{sublimation}H_m^4$	1	5.180637	5.18063742
23	$\Delta_{sublimation}H_m^{23}$	1	2.102287	2.102286687
24	$\Delta_{sublimation}H_m^{24}$	1	-10.1085	-10.10848286
39	$\Delta_{sublimation}H_m^{39}$	1	59.12675	59.12674626
49	$\Delta_{sublimation}H_m^{49}$	13	-0.11698	-1.520792582
50	$\Delta_{sublimation}H_m^{50}$	1	1.524469	1.524468656
51	$\Delta_{sublimation}H_m^{51}$	1	-41.7694	-41.76940137

66	$\Delta_{sublimation}H_m^{66}$	1	-5.34759	-5.347590443
68	$\Delta_{sublimation}H_m^{68}$	1	1.167072	1.167072277
69	$\Delta_{sublimation}H_m^{69}$	1	13.44807	13.44806904
73	$\Delta_{sublimation}H_m^{73}$	1	-6.3383	-6.338298652
75	$\Delta_{sublimation}H_m^{75}$	1	-2.32134	-2.321344256
78	$\Delta_{sublimation}H_m^{78}$	1	1.067491	1.067491379
80	$\Delta_{sublimation}H_m^{80}$	1	-1.53055	-1.530549801
111	$\Delta_{sublimation}H_m^{111}$	11	5.538397	60.92236595
113	$\Delta_{sublimation}H_m^{113}$	1	7.904142	7.904142211
119	$\Delta_{sublimation}H_m^{119}$	16	-2.11715	-33.87436543
121	$\Delta_{sublimation}H_m^{121}$	2	-1.40174	-2.803484879
123	$\Delta_{sublimation}H_m^{123}$	13	1.344881	17.48345031
126	$\Delta_{sublimation}H_m^{126}$	5	-1.13923	-5.696139159
128	$\Delta_{sublimation}H_m^{128}$	2	-1.02864	-2.057274921
	Sum			82.74

Example 2:
2-phenyl-4H-1-benzopyran-4-one (flavone)



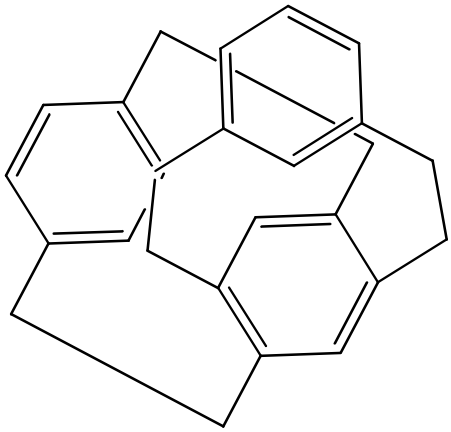
Experimental value: 108.2±1.7 kJ.mole^{-1}

Predicted value: 110.75 kJ.mole^{-1} (2.4% deviation)

ID	$\Delta_{Sublimation}H_m^{i}$	Number	Value	Number X VALUE
	$\Delta_{sublimation}H_m^{0}$		17.22157658	17.22157658
5	$\Delta_{sublimation}H_m^{5}$	12	2.327303476	27.92764171
6	$\Delta_{sublimation}H_m^{6}$	3	-2.84795394	-8.54386182
7	$\Delta_{sublimation}H_m^{7}$	3	1.719792347	5.159377041
26	$\Delta_{sublimation}H_m^{26}$	1	5.235888943	5.235888943
42	$\Delta_{sublimation}H_m^{42}$	1	-1.786805532	-1.786805532

43	$\Delta_{sublimation}H_m^{43}$	9	-1.949630378	-17.5466734
44	$\Delta_{sublimation}H_m^{44}$	2	3.237334284	6.474668567
50	$\Delta_{sublimation}H_m^{50}$	10	1.524468656	15.24468656
53	$\Delta_{sublimation}H_m^{53}$	1	4.370113154	4.370113154
54	$\Delta_{sublimation}H_m^{54}$	1	-4.089886384	-4.089886384
66	$\Delta_{sublimation}H_m^{66}$	1	-5.347590443	-5.347590443
68	$\Delta_{sublimation}H_m^{68}$	1	1.167072277	1.167072277
69	$\Delta_{sublimation}H_m^{69}$	1	13.44806904	13.44806904
73	$\Delta_{sublimation}H_m^{73}$	1	-6.338298652	-6.338298652
75	$\Delta_{sublimation}H_m^{75}$	1	-2.321344256	-2.321344256
78	$\Delta_{sublimation}H_m^{78}$	1	1.067491379	1.067491379
79	$\Delta_{sublimation}H_m^{79}$	1	0.360241352	0.360241352
80	$\Delta_{sublimation}H_m^{80}$	1	-1.530549801	-1.530549801
94	$\Delta_{sublimation}H_m^{94}$	1	1.26499858	1.26499858
95	$\Delta_{sublimation}H_m^{95}$	1	-1.389579357	-1.389579357
102	$\Delta_{sublimation}H_m^{102}$	1	0.778841644	0.778841644
111	$\Delta_{sublimation}H_m^{111}$	16	5.538396905	88.61435047
113	$\Delta_{sublimation}H_m^{113}$	3	7.904142211	23.71242663
119	$\Delta_{sublimation}H_m^{119}$	20	-2.117147839	-42.34295679
121	$\Delta_{sublimation}H_m^{121}$	6	-1.401742439	-8.410454636
123	$\Delta_{sublimation}H_m^{123}$	18	1.344880793	24.20785428
126	$\Delta_{sublimation}H_m^{126}$	14	-1.139227832	-15.94918964
128	$\Delta_{sublimation}H_m^{128}$	6	-1.028637461	-6.171824764
133	$\Delta_{sublimation}H_m^{133}$	13	-0.268166117	-3.486159527
145	$\Delta_{sublimation}H_m^{145}$	1	-0.251418535	-0.251418535
	Sum			110.75

Example 3:
pentacyclo[18.2.2.2(9,12).0(4,15).0(4,15).0(6,17)]hexacos-4,6(17),9,11,-15,20,22,23,25-nonane (triple layered [2.2]paracyclophane)



Experimental value: 125.9±2.5 kJ.mole^{-1}

Predicted value: 132.77 kJ.mole^{-1} (5.5% deviation)

ID	$\Delta_{Sublimation}H_m^i$	Number	Value	Number X VALUE
	$\Delta_{sublimation}H_m^0$		17.22157658	17.22157658
2	$\Delta_{sublimation}H_m^2$	8	4.324474902	34.59579921
3	$\Delta_{sublimation}H_m^3$	8	-3.176569198	-25.41255358
5	$\Delta_{sublimation}H_m^5$	18	2.327303476	41.89146256
6	$\Delta_{sublimation}H_m^6$	8	-2.84795394	-22.78363152
43	$\Delta_{sublimation}H_m^{43}$	10	-1.949630378	-19.49630378
44	$\Delta_{sublimation}H_m^{44}$	8	3.237334284	25.89867427
49	$\Delta_{sublimation}H_m^{49}$	16	-0.116984045	-1.871744717
50	$\Delta_{sublimation}H_m^{50}$	10	1.524468656	15.24468656
68	$\Delta_{sublimation}H_m^{68}$	1	1.167072277	1.167072277
73	$\Delta_{sublimation}H_m^{73}$	1	-6.338298652	-6.338298652
79	$\Delta_{sublimation}H_m^{79}$	1	0.360241352	0.360241352
94	$\Delta_{sublimation}H_m^{94}$	1	1.26499858	1.26499858
102	$\Delta_{sublimation}H_m^{102}$	1	0.778841644	0.778841644
108	$\Delta_{sublimation}H_m^{108}$	1	2.124815779	2.124815779
111	$\Delta_{sublimation}H_m^{111}$	30	5.538396905	166.1519071
119	$\Delta_{sublimation}H_m^{119}$	42	-2.117147839	-88.92020925
123	$\Delta_{sublimation}H_m^{123}$	47	1.344880793	63.20939728
126	$\Delta_{sublimation}H_m^{126}$	47	-1.139227832	-53.54370809
133	$\Delta_{sublimation}H_m^{133}$	55	-0.268166117	-14.74913646
145	$\Delta_{sublimation}H_m^{145}$	16	-0.251418535	-4.022696558
	Sum			132.77

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Figure Captions

Figure 1- The gradual change of R^2 *and ARD%* as function of number of chemical substructures.

Figure 2- Williams plot – red circles shows the outliers of the model for which the experimental values may be erroneous.

Figure 3- The sublimation enthalpies of hydrocarbons predicted by the model vs. experimental data. The left side (o) should be read for R^2 and the right side (+) should be read for *RD%*

Figure 4- The sublimation enthalpies of nitrogen compounds predicted by the model vs. experimental data. The left side (o) should be read for R^2 and the right side (+) should be read for *RD%*

Figure 5- The sublimation enthalpies of oxygen compounds predicted by the model vs. experimental data. The left side (o) should be read for R^2 and the right side (+) should be read for *RD%*

Figure 6- The sublimation enthalpies of sulfur compounds predicted by the model vs. experimental data. The left side (o) should be read for R^2 and the right side (+) should be read for *RD%*

Figure 7- The sublimation enthalpies of fluorine compounds predicted by the model vs. experimental data. The left side (o) should be read for R^2 and the right side (+) should be read for *RD%*

Figure 8- The sublimation enthalpies of chlorine compounds predicted by the model vs. experimental data. The left side (o) should be read for R^2 and the right side (+) should be read for *RD%*

Figure 9- The sublimation enthalpies of bromine compounds predicted by the model vs. experimental data. The left side (o) should be read for R^2 and the right side (+) should be read for *RD%*

Figure 10- The sublimation enthalpies of iodine compounds predicted by the model vs. experimental data. The left side (o) should be read for R^2 and the right side (+) should be read for *RD%*

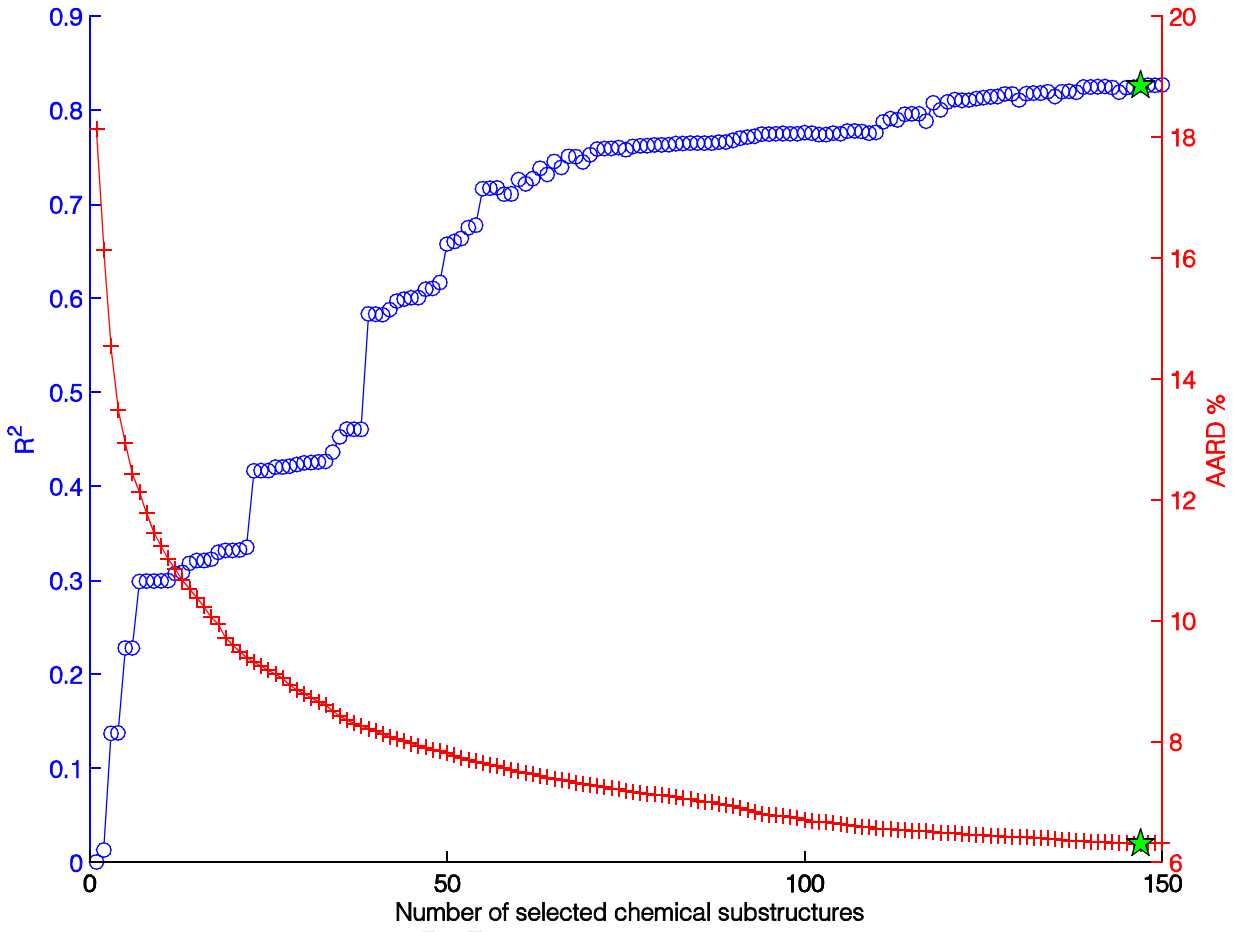


Figure 1.

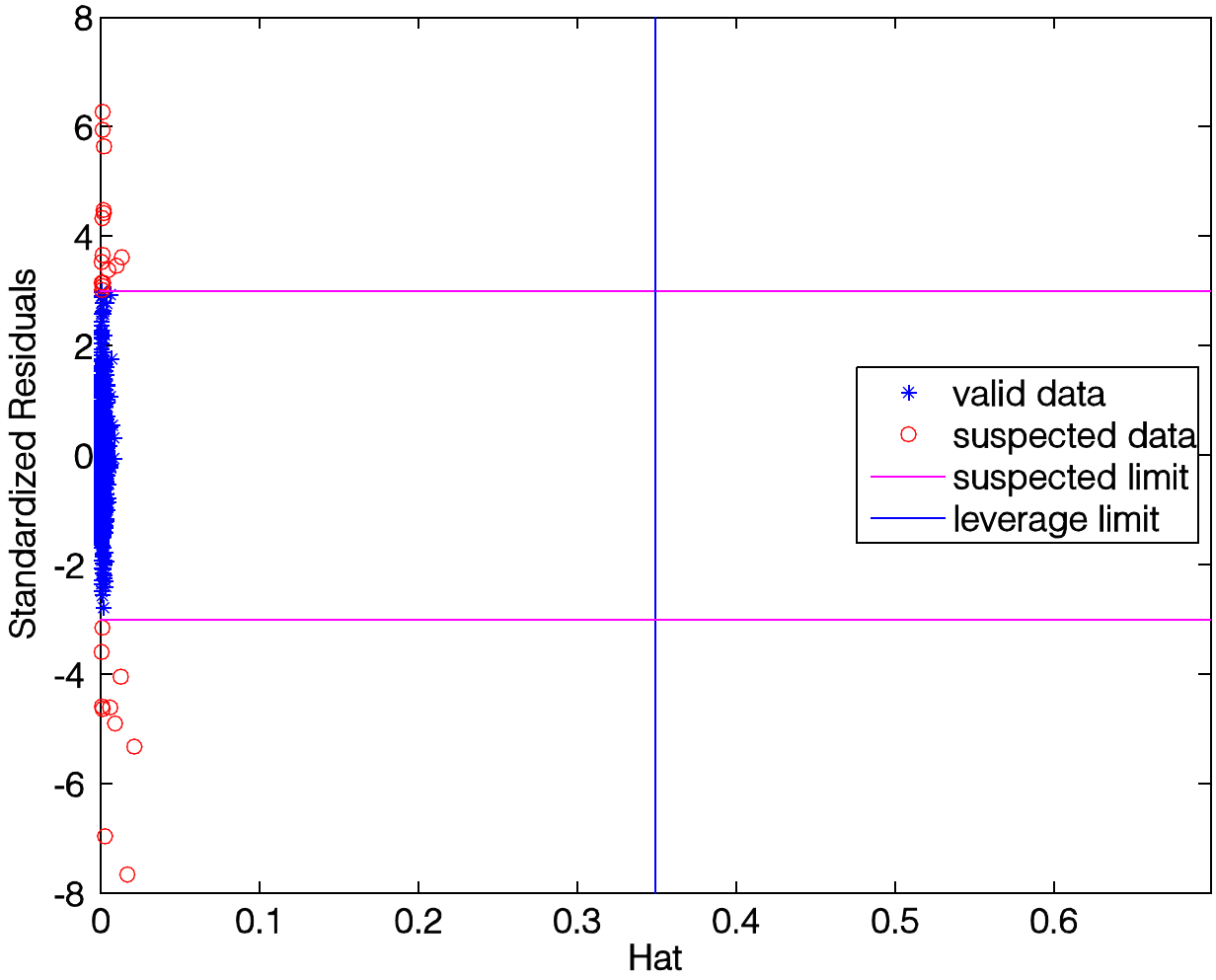


Figure 2.

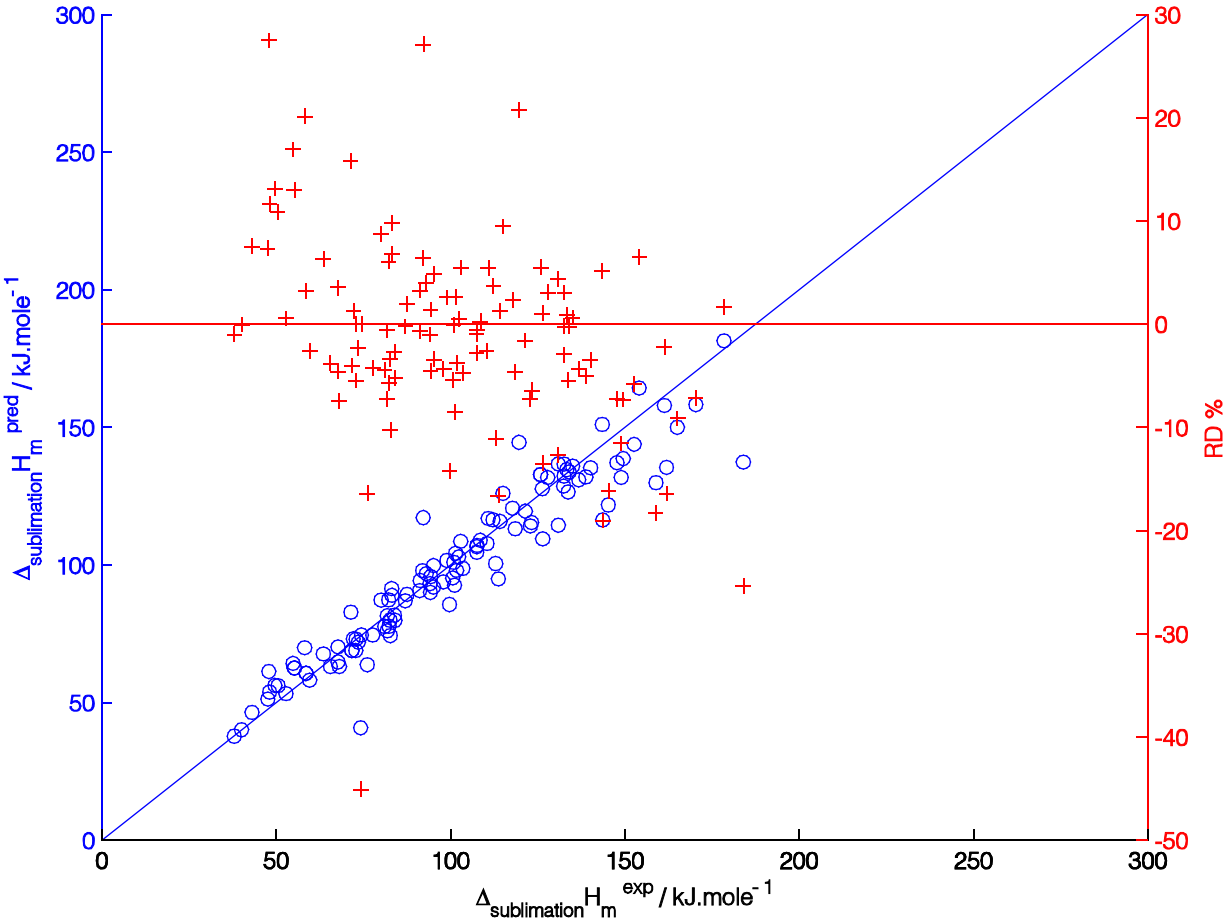


Figure 3.

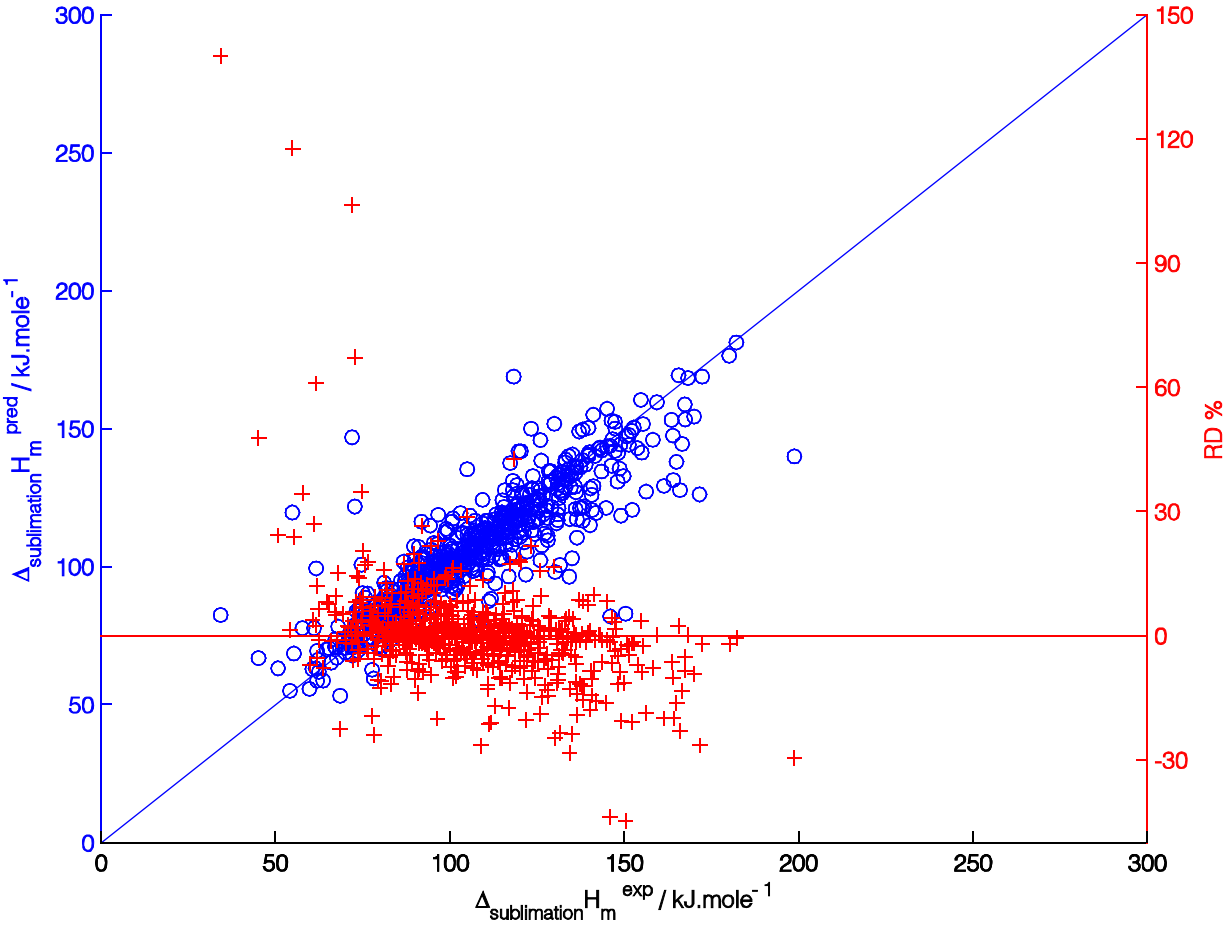


Figure 4.

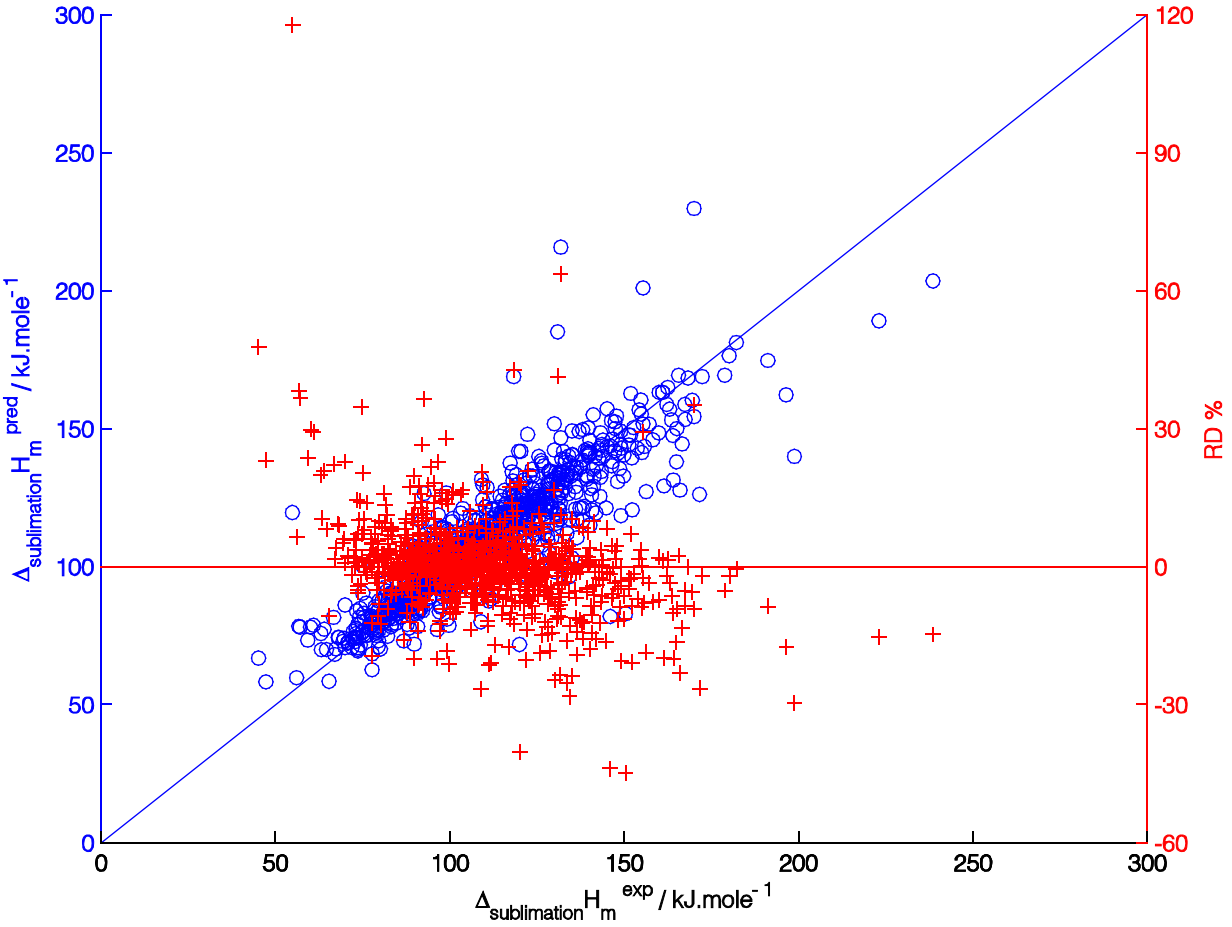


Figure 5.

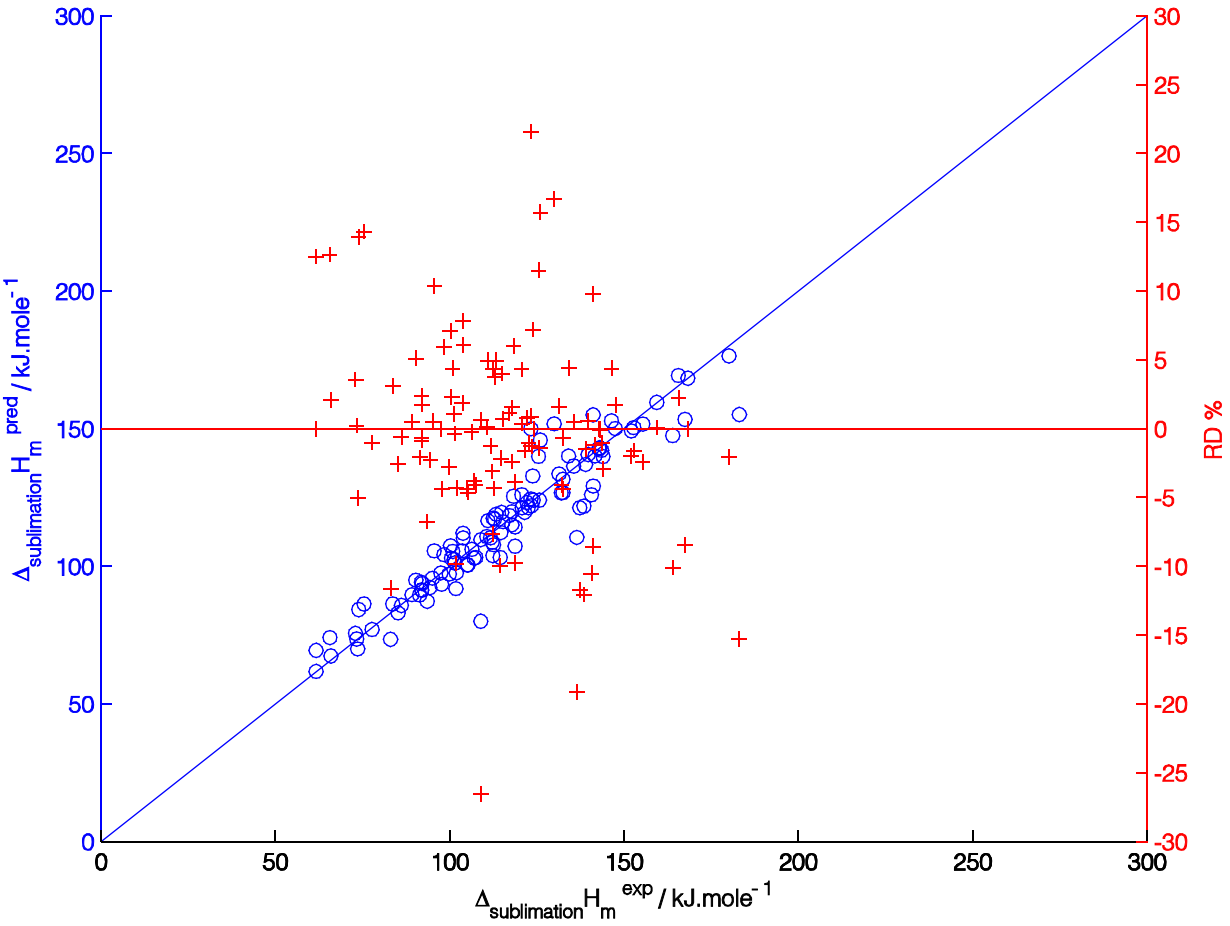


Figure 6.

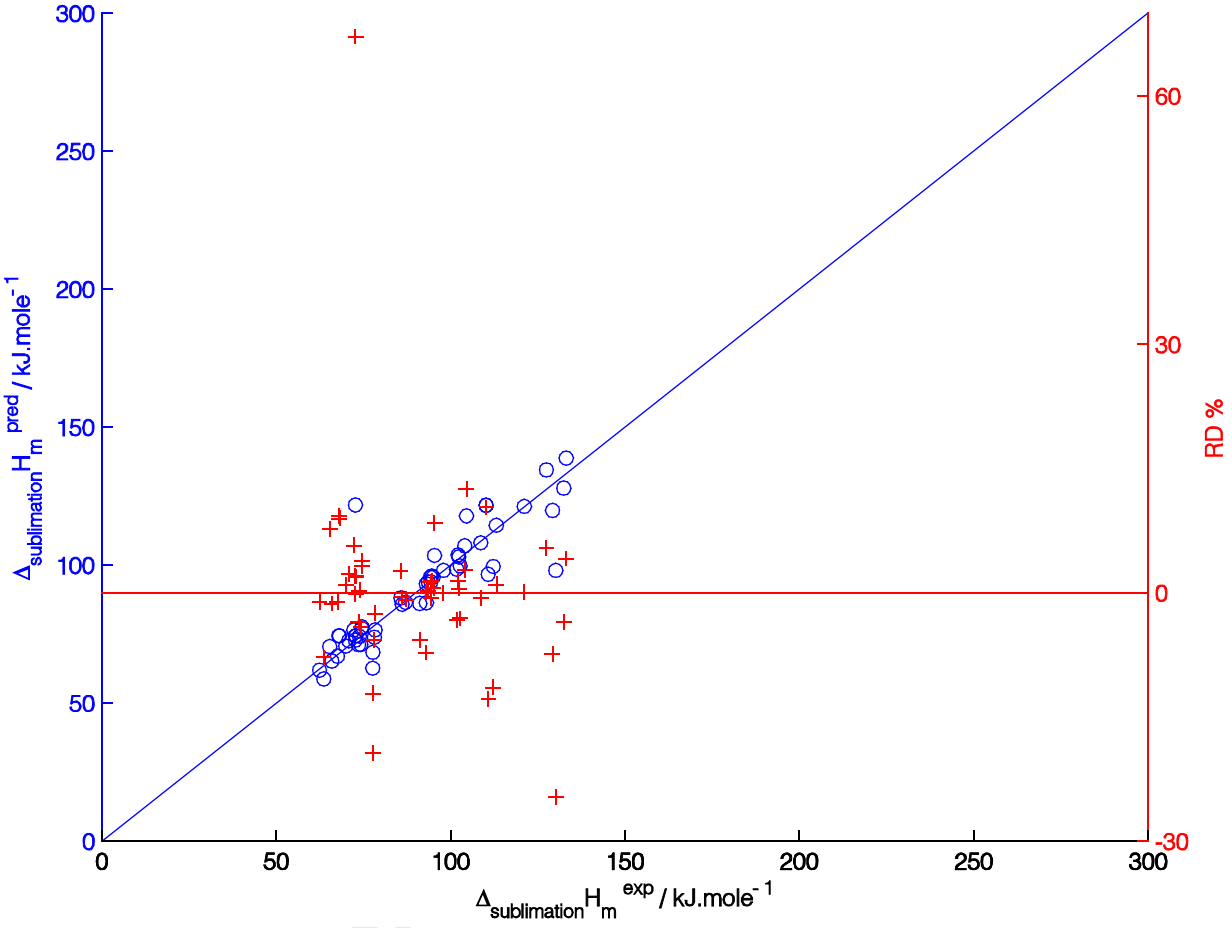
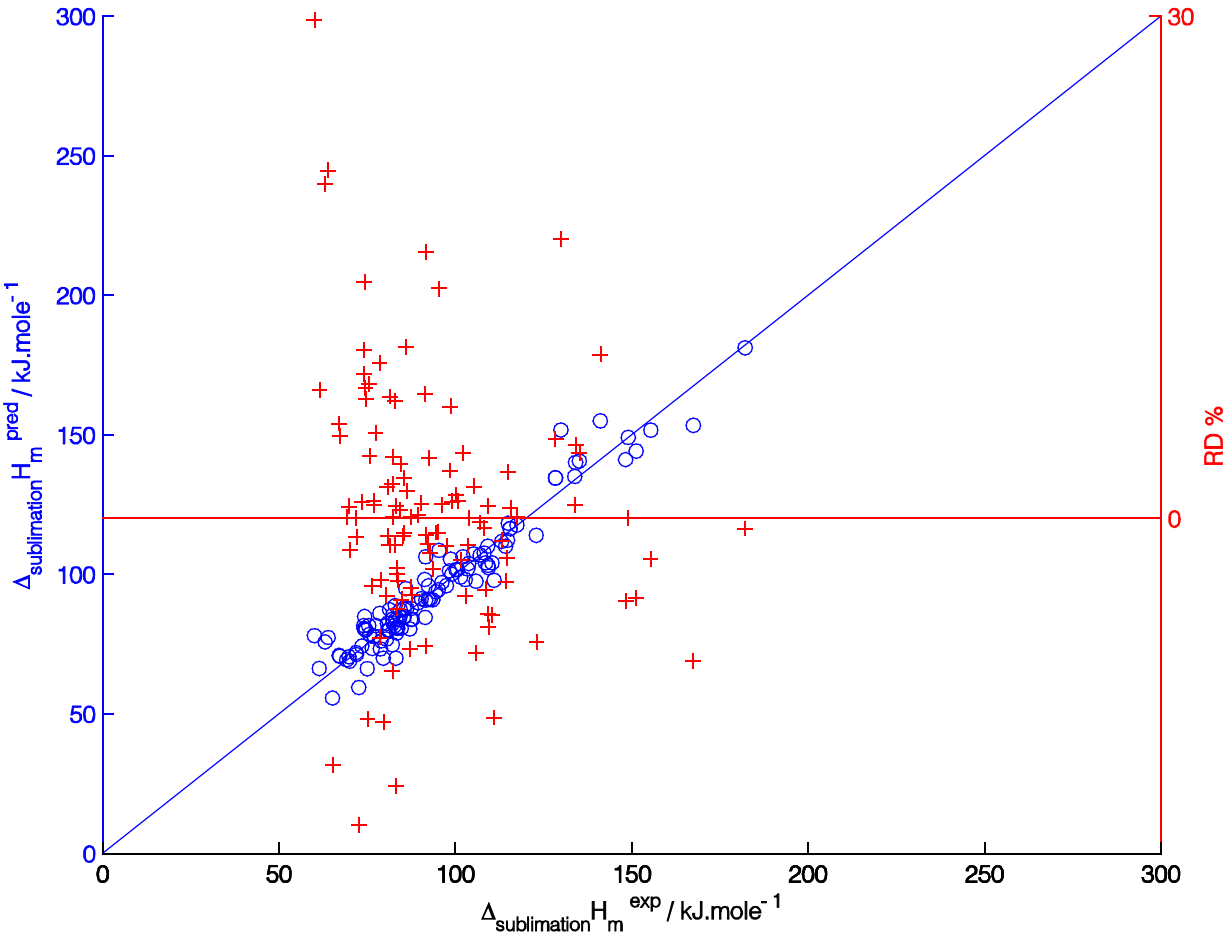


Figure 7.



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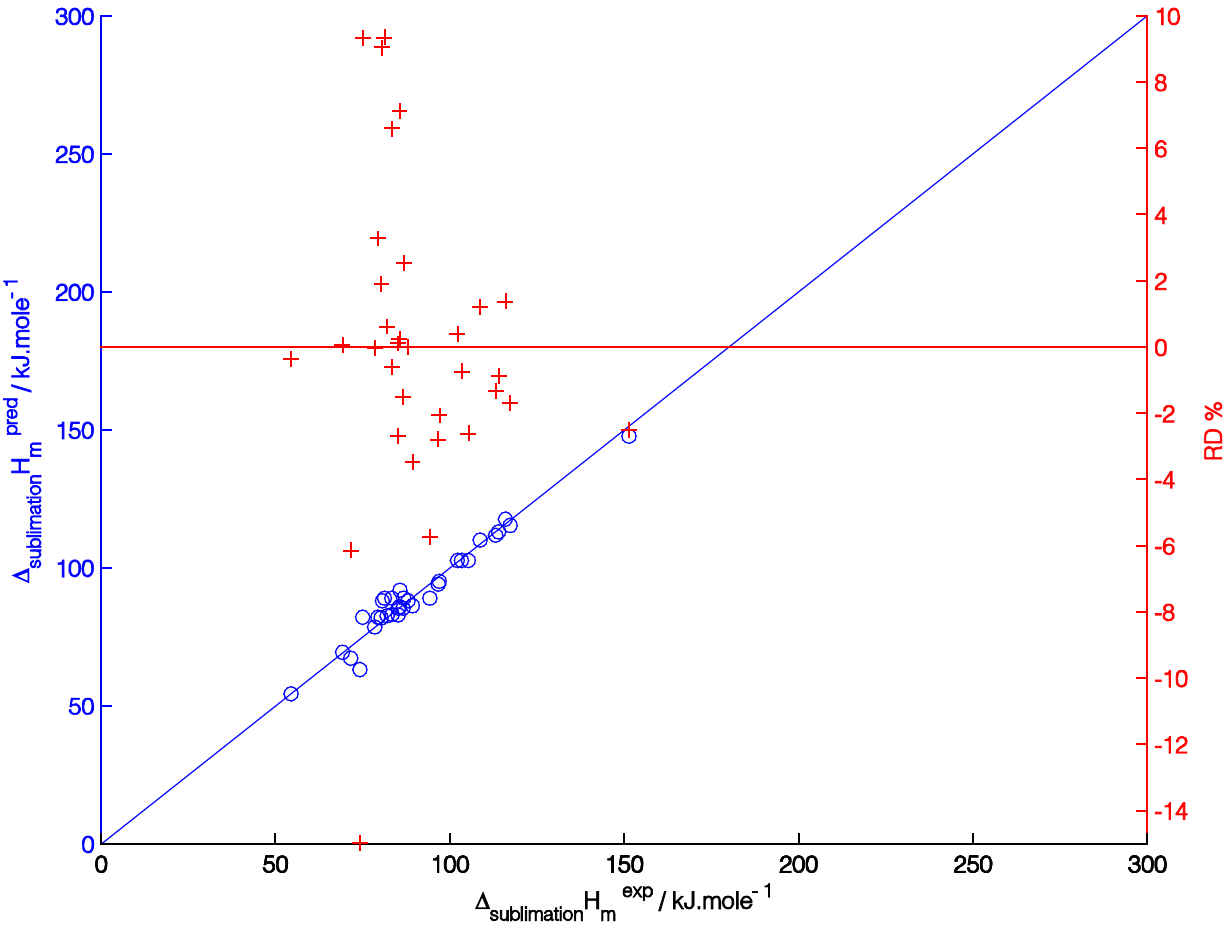


Figure 9.

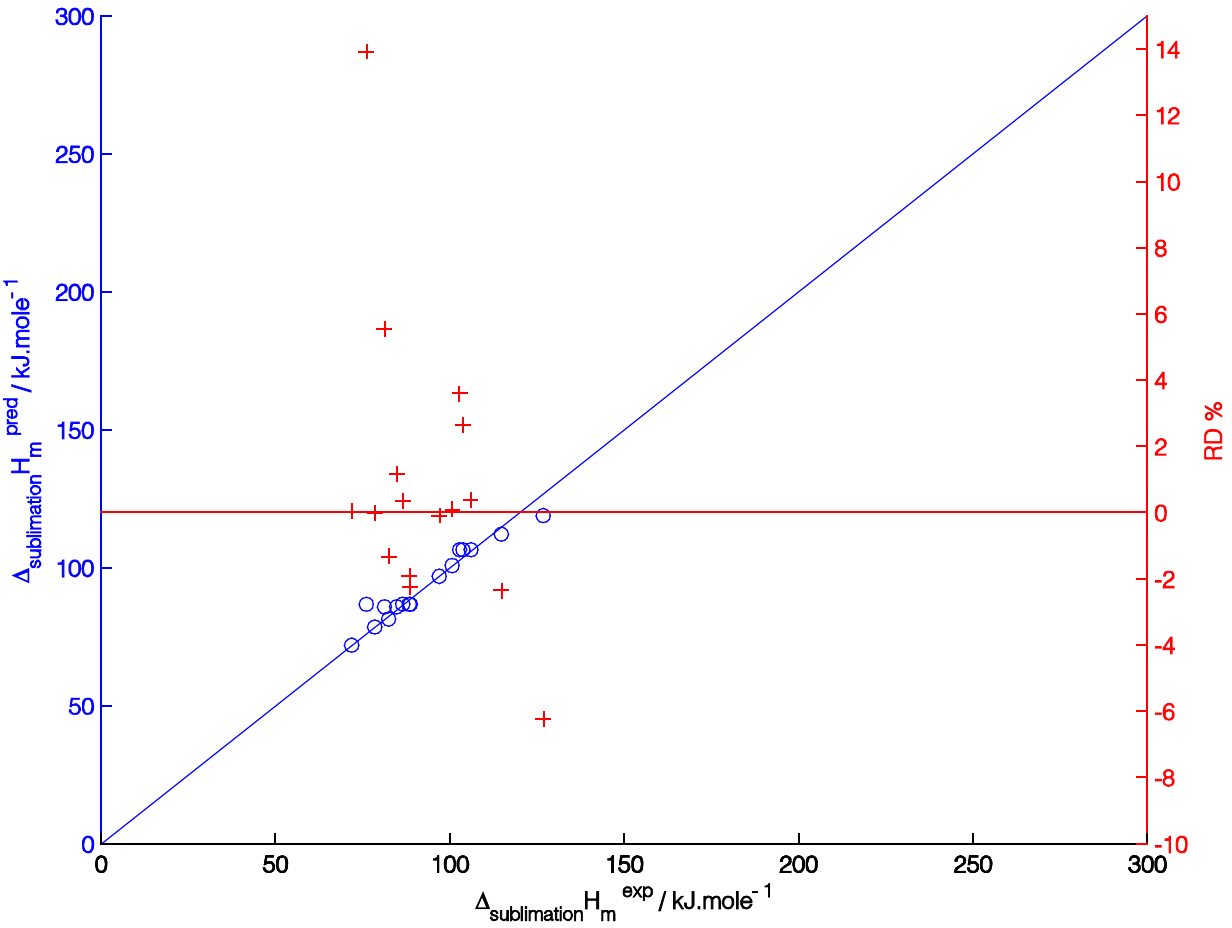
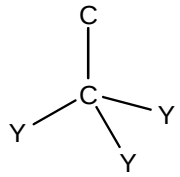
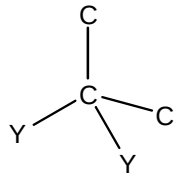
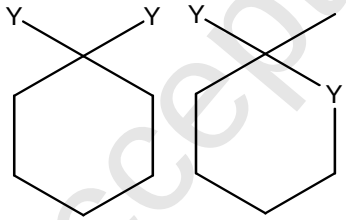
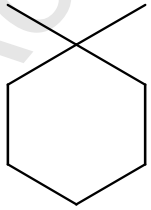
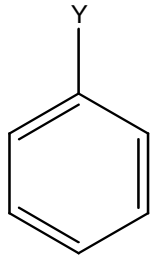
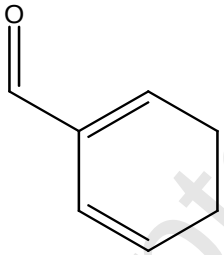
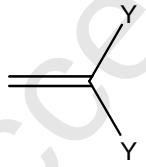
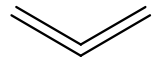
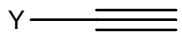
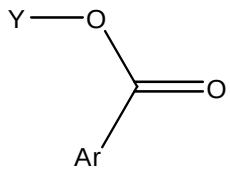
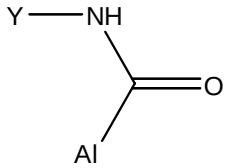
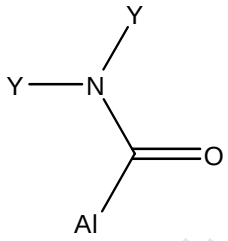
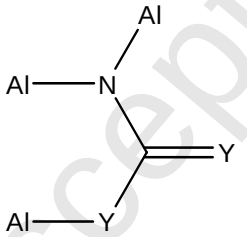
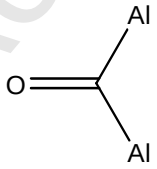


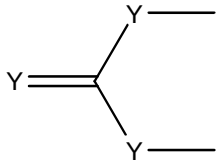
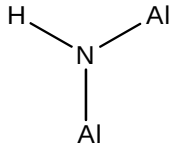
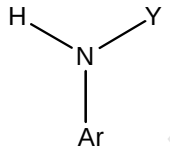
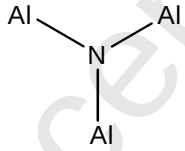
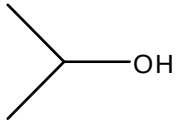
Figure 10.

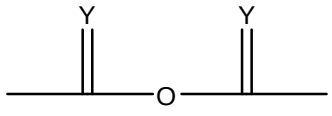
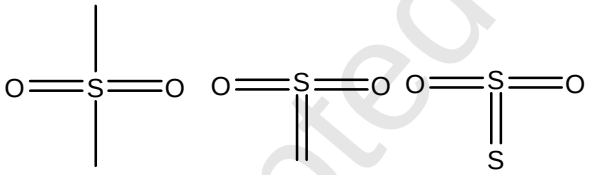
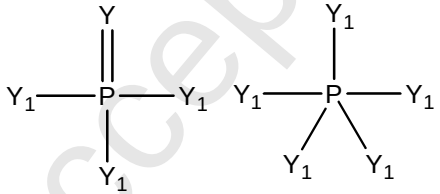
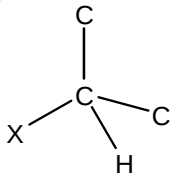
Table 1- The contribution of each chemical substructure to the sublimation enthalpy of organic compounds (parameters of eq. (2)).

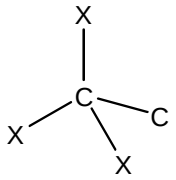
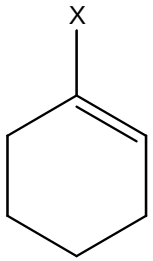
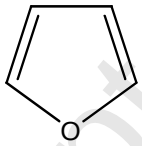
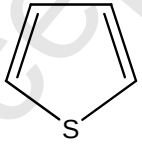
ID	$\Delta_{Sublimation}H_m^i$	Chemical substructure	Comment	Value
	$\Delta_{sublimation}H_m^0$			17.22158
1	$\Delta_{sublimation}H_m^1$		number of terminal primary C(sp3) Y = any terminal atom or heteroaromatic group (i.e. H, X, OH, NH2, etc.)	1.839585
2	$\Delta_{sublimation}H_m^2$		number of total secondary C(sp3) Y = H or any heteroatom	4.324475
3	$\Delta_{sublimation}H_m^3$		number of ring secondary C(sp3) Y = H or any heteroatom	-3.17657
4	$\Delta_{sublimation}H_m^4$		number of ring quaternary C(sp3)	5.180637

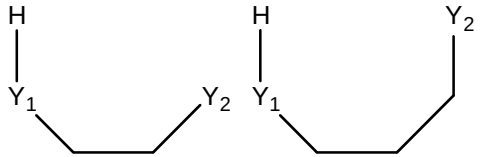
5	$\Delta_{sublimation}H_m^5$	Sum of all the carbons belonging to any aromatic and heteroaromatic structure	number of aromatic C(sp2)	2.327303
6	$\Delta_{sublimation}H_m^6$		number of substituted benzene C(sp2) Y = carbon or any heteroatom	-2.84795
7	$\Delta_{sublimation}H_m^7$		number of non-aromatic conjugated C(sp2)	1.719792
8	$\Delta_{sublimation}H_m^8$		number of terminal primary C(sp2) Y = any terminal atom or heteroaromatic group (i.e. H, X, OH, NH2, etc.)	-3.80592
9	$\Delta_{sublimation}H_m^9$		number of allenes groups	11.52741
10	$\Delta_{sublimation}H_m^{10}$		number of non-terminal C(sp) Y = C or any non-terminal heteroatom	5.037913

11	$\Delta_{sublimation}H_m^{11}$		number of esters (aromatic) Y = Al or Ar	-2.10042
12	$\Delta_{sublimation}H_m^{12}$		number of secondary amides (aliphatic) Y = Ar or Al (not H, not C = O) Al = H or aliphatic group linked through C	7.354295
13	$\Delta_{sublimation}H_m^{13}$		number of tertiary amides (aliphatic) Y = Ar or Al (not H, not C = O) Al = H or aliphatic group linked through C	12.00637
14	$\Delta_{sublimation}H_m^{14}$		number of (thio-) carbamates (aliphatic) Y = O or S Al = H or aliphatic group linked through any atom	-10.6307
15	$\Delta_{sublimation}H_m^{15}$		number of ketones (aliphatic)	3.564898

16	$\Delta_{sublimation}H_m^{16}$			number of carbonate (-thio) derivatives Y = O or S	-10.5264
17	$\Delta_{sublimation}H_m^{17}$		Ar-NH_2	number of primary amines (aromatic)	-16.3392
18	$\Delta_{sublimation}H_m^{18}$			number of secondary amines (aliphatic) Al = aliphatic group linked through C (not C = O)	-32.4857
19	$\Delta_{sublimation}H_m^{19}$			number of secondary amines (aromatic) Y = Ar or Al (not C = O)	-17.7938
20	$\Delta_{sublimation}H_m^{20}$			number of tertiary amines (aliphatic) Al = aliphatic group linked through C (not C = O)	-10.6959
21	$\Delta_{sublimation}H_m^{21}$	Ar-CN		number of nitriles (aromatic)	3.199378
22	$\Delta_{sublimation}H_m^{22}$	>N<		number of quaternary N	-19.5828
23	$\Delta_{sublimation}H_m^{23}$	Al-OH		number of hydroxyl groups Al = aliphatic group linked through any atom	2.102287
24	$\Delta_{sublimation}H_m^{24}$			number of secondary alcohols	-10.1085

25	$\Delta_{sublimation}H_m^{25}$	Al-O-Al	number of ethers (aliphatic) Al = aliphatic group linked through C (not C = O, not C # N)	-4.02326
26	$\Delta_{sublimation}H_m^{26}$	Ar-O-Y	number of ethers (aromatic) Y = Ar or Al (not C = O, not C # N)	5.235889
27	$\Delta_{sublimation}H_m^{27}$		number of anhydrides (thio-) Y = O or S	12.35995
28	$\Delta_{sublimation}H_m^{28}$	S=C<	number of thioketones	-29.7795
29	$\Delta_{sublimation}H_m^{29}$	-S-	number of sulfides	-11.2922
30	$\Delta_{sublimation}H_m^{30}$	-S-S-	number of disulfides	5.389454
31	$\Delta_{sublimation}H_m^{31}$		number of sulfones	9.439112
32	$\Delta_{sublimation}H_m^{32}$		number of phosphoranes / thiophosphoranes Y = O or S	17.70081
33	$\Delta_{sublimation}H_m^{33}$		number of CHR_2X	-6.79778

34	$\Delta_{sublimation}H_m^{34}$			number of CRX_3	-9.81816
35	$\Delta_{sublimation}H_m^{35}$	Ar-X		number of X on aromatic ring	3.208322
36	$\Delta_{sublimation}H_m^{36}$			number of X on ring C(sp2)	22.24842
37	$\Delta_{sublimation}H_m^{37}$			number of Furanes	-1.45294
38	$\Delta_{sublimation}H_m^{38}$			number of Thiophenes	-16.1342
39	$\Delta_{sublimation}H_m^{39}$	Sum of the hydrogens linked to all of the Os and Ns in the molecule		number of donor atoms for H-bonds (N and O)	59.12675

40	$\Delta_{sublimation}H_m^{40}$		number of intramolecular H-bonds Y1 = B, N, O, Al, P, S Y2 = N, O, F The geometric distance between H and Y2 must be in the range 1 - 2,7 A.	-5.99035
41	$\Delta_{sublimation}H_m^{41}$	CH2X2		5.988704
42	$\Delta_{sublimation}H_m^{42}$	=CHR		-1.78681
43	$\Delta_{sublimation}H_m^{43}$	R--CH--R		-1.94963
44	$\Delta_{sublimation}H_m^{44}$	R--CR--R		3.237334
45	$\Delta_{sublimation}H_m^{45}$	X--CH--X		-6.81541
46	$\Delta_{sublimation}H_m^{46}$	X--CX--X		-8.72027
47	$\Delta_{sublimation}H_m^{47}$	R-C(=X)-X or R-C#X or X=C=X		0.085745
48	$\Delta_{sublimation}H_m^{48}$	X--CX..X		-13.0023
49	$\Delta_{sublimation}H_m^{49}$	H^a attached to C^0(sp3) no X attached to next C		-0.11698
50	$\Delta_{sublimation}H_m^{50}$	H^a attached to C^1(sp3) or C^0(sp2)		1.524469
51	$\Delta_{sublimation}H_m^{51}$	H attached to heteroatom		-41.7694
52	$\Delta_{sublimation}H_m^{52}$	H^a attached to C^0(sp3) with 2X attached to next C		-1.16842
53	$\Delta_{sublimation}H_m^{53}$	=O		4.370113
54	$\Delta_{sublimation}H_m^{54}$	Al-O-Ar or Ar-O-Ar or R..O..R or R-O-C=X		-4.08989
55	$\Delta_{sublimation}H_m^{55}$	O-- [b]		2.422218
56	$\Delta_{sublimation}H_m^{56}$	O^- (negatively charged)		23.85644
57	$\Delta_{sublimation}H_m^{57}$	R-O-O-R		11.10866
58	$\Delta_{sublimation}H_m^{58}$	Al_2-NH		17.85208
59	$\Delta_{sublimation}H_m^{59}$	Ar-NH-Al		7.191607
60	$\Delta_{sublimation}H_m^{60}$	RCO-N< or >N-X=X		-7.10496
61	$\Delta_{sublimation}H_m^{61}$	R#N or R=N-		3.820022
62	$\Delta_{sublimation}H_m^{62}$	Ar-NO_2 or R--N(--R)--O^c or RO-NO		10.98812
63	$\Delta_{sublimation}H_m^{63}$	F^a attached to $C^1(sp^2)$		-0.59666

64	$\Delta_{sublimation}H_m^{64}$	Br[a] attached to $C^2(sp^2)$-$C^4(sp^2)$ or $C^1(sp)$ or $C^4(sp^3)$ or X		3.598674
65	$\Delta_{sublimation}H_m^{65}$	R-SH		62.64204
66	$\Delta_{sublimation}H_m^{66}$	presence (0) or absence (1) of C-O		-5.34759
67	$\Delta_{sublimation}H_m^{67}$	presence (0) or absence (1) of N-P		-65.8101
68	$\Delta_{sublimation}H_m^{68}$	presence (0) or absence (1) of C-A-C	A means any atom	1.167072
69	$\Delta_{sublimation}H_m^{69}$	presence (0) or absence (1) of C-A-O	A means any atom	13.44807
70	$\Delta_{sublimation}H_m^{70}$	presence (0) or absence (1) of C-A-Br	A means any atom	3.07181
71	$\Delta_{sublimation}H_m^{71}$	presence (0) or absence (1) of N-A-N	A means any atom	11.17699
72	$\Delta_{sublimation}H_m^{72}$	presence (0) or absence (1) of N-A-N	A means any atom	2.047634
73	$\Delta_{sublimation}H_m^{73}$	presence (0) or absence (1) of C-A1-A2-C	A1 and A2 means any atom	-6.3383
74	$\Delta_{sublimation}H_m^{74}$	presence (0) or absence (1) of C-A1-A2-N	A1 and A2 means any atom	5.717817
75	$\Delta_{sublimation}H_m^{75}$	presence (0) or absence (1) of C-A1-A2-O	A1 and A2 means any atom	-2.32134
76	$\Delta_{sublimation}H_m^{76}$	presence (0) or absence (1) of C-A1-A2-S	A1 and A2 means any atom	6.836506
77	$\Delta_{sublimation}H_m^{77}$	presence (0) or absence (1) of C-A1-A2-A3-N	A1 , A2 and A3, means any atom	-1.9211
78	$\Delta_{sublimation}H_m^{78}$	presence (0) or absence (1) of C-A1-A2-A3-O	A1 , A2 and A3, means any atom	1.067491
79	$\Delta_{sublimation}H_m^{79}$	presence (0) or absence (1) of C-A1-A2-A3-A4-C	A1 , A2 , A3, and A4 means any atom	0.360241
80	$\Delta_{sublimation}H_m^{80}$	presence (0) or absence (1) of C-A1-A2-A3-A4-O	A1 , A2 , A3, and A4 means any atom	-1.53055
81	$\Delta_{sublimation}H_m^{81}$	presence (0) or absence (1) of C-A1-A2-A3-A4-S	A1 , A2 , A3, and A4 means any atom	-6.38755
82	$\Delta_{sublimation}H_m^{82}$	presence (0) or absence (1) of N-A1-A2-A3-A4-O	A1 , A2 , A3, and A4 means any atom	0.519688
83	$\Delta_{sublimation}H_m^{83}$	presence (0) or absence (1) of N-A1-A2-A3-A4-F	A1 , A2 , A3, and A4 means any atom	7.439548
84	$\Delta_{sublimation}H_m^{84}$	presence (0) or absence (1) of O-A1-A2-A3-A4-O	A1 , A2 , A3, and A4 means any atom	5.36676
85	$\Delta_{sublimation}H_m^{85}$	presence (0) or absence (1) of Cl-A1-A2-A3-A4-Br	A1 , A2 , A3, and A4 means any atom	8.366331
86	$\Delta_{sublimation}H_m^{86}$	presence (0) or absence (1) of Cl-A1-A2-A3-A4-I	A1 , A2 , A3, and A4 means any atom	7.186903
87	$\Delta_{sublimation}H_m^{87}$	presence (0) or absence (1) of Br-A1-A2-A3-A4-I	A1 , A2 , A3, and A4 means any atom	8.570828
88	$\Delta_{sublimation}H_m^{88}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-S	A1 , A2 , A3, A4 and A5 means any atom	-5.59339
89	$\Delta_{sublimation}H_m^{89}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-Br	A1 , A2 , A3, A4 and A5 means any atom	-0.37507
90	$\Delta_{sublimation}H_m^{90}$	presence (0) or absence (1) of N-A1-A2-A3-A4-A5-Cl	A1 , A2 , A3, A4 and A5 means any atom	27.02776
91	$\Delta_{sublimation}H_m^{91}$	presence (0) or absence (1) of O-A1-A2-A3-A4-A5-O	A1 , A2 , A3, A4 and A5 means any atom	5.795304

92	$\Delta_{sublimation}H_m^{92}$	presence (0) or absence (1) of O-A1-A2-A3-A4-A5-S	A1 , A2 , A3, A4 and A5 means any atom	-25.9605
93	$\Delta_{sublimation}H_m^{93}$	presence (0) or absence (1) of S-A1-A2-A3-A4-A5-F	A1 , A2 , A3, A4 and A5 means any atom	-16.4801
94	$\Delta_{sublimation}H_m^{94}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-C	A1 , A2 , A3, A4 ,A5 and A6 means any atom	1.264999
95	$\Delta_{sublimation}H_m^{95}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-O	A1 , A2 , A3, A4 ,A5 and A6 means any atom	-1.38958
96	$\Delta_{sublimation}H_m^{96}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-F	A1 , A2 , A3, A4 ,A5 and A6 means any atom	4.043397
97	$\Delta_{sublimation}H_m^{97}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-I	A1 , A2 , A3, A4 ,A5 and A6 means any atom	6.879248
98	$\Delta_{sublimation}H_m^{98}$	presence (0) or absence (1) of N-A1-A2-A3-A4-A5-A6-N	A1 , A2 , A3, A4 ,A5 and A6 means any atom	6.246321
99	$\Delta_{sublimation}H_m^{99}$	presence (0) or absence (1) of N-A1-A2-A3-A4-A5-A6-S	A1 , A2 , A3, A4 ,A5 and A6 means any atom	82.38669
100	$\Delta_{sublimation}H_m^{100}$	presence (0) or absence (1) of N-A1-A2-A3-A4-A5-A6-F	A1 , A2 , A3, A4 ,A5 and A6 means any atom	-36.297
101	$\Delta_{sublimation}H_m^{101}$	presence (0) or absence (1) of O-A1-A2-A3-A4-A5-A6-O	A1 , A2 , A3, A4 ,A5 and A6 means any atom	6.121689
102	$\Delta_{sublimation}H_m^{102}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-A7-C	A1 , A2 , A3, A4 ,A5 ,A6 and A7 means any atom	0.778842
103	$\Delta_{sublimation}H_m^{103}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-A7-O	A1 , A2 , A3, A4 ,A5 ,A6 and A7 means any atom	-1.67133
104	$\Delta_{sublimation}H_m^{104}$	presence (0) or absence (1) of N-A1-A2-A3-A4-A5-A6-A7-N	A1 , A2 , A3, A4 ,A5 ,A6 and A7 means any atom	36.78154
105	$\Delta_{sublimation}H_m^{105}$	presence (0) or absence (1) of O-A1-A2-A3-A4-A5-A6-A7-O	A1 , A2 , A3, A4 ,A5 ,A6 and A7 means any atom	7.876963
106	$\Delta_{sublimation}H_m^{106}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-A7-A8-S	A1 , A2 , A3, A4 ,A5 ,A6 ,A7 and A8 means any atom	30.18888
107	$\Delta_{sublimation}H_m^{107}$	presence (0) or absence (1) of Cl-A1-A2-A3-A4-A5-A6-A7-A8-Cl	A1 , A2 , A3, A4 ,A5 ,A6 ,A7 and A8 means any atom	12.66579
108	$\Delta_{sublimation}H_m^{108}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-A7-A8-A9-C	A1 , A2 , A3, A4 ,A5 ,A6 ,A7, A8 and A9 means any atom	2.124816
109	$\Delta_{sublimation}H_m^{109}$	presence (0) or absence (1) of C-A1-A2-A3-A4-A5-A6-A7-A8-A9-S	A1 , A2 , A3, A4 ,A5 ,A6 ,A7, A8 and A9 means any atom	11.74033
110	$\Delta_{sublimation}H_m^{110}$	presence (0) or absence (1) of O-A1-A2-A3-A4-A5-A6-A7-A8-A9-Cl	A1 , A2 , A3, A4 ,A5 ,A6 ,A7, A8 and A9 means any atom	15.2838
111	$\Delta_{sublimation}H_m^{111}$	number of C-C		5.538397
112	$\Delta_{sublimation}H_m^{112}$	number of C-N		7.531674
113	$\Delta_{sublimation}H_m^{113}$	number of C-O		7.904142
114	$\Delta_{sublimation}H_m^{114}$	number of C-S		14.03693
115	$\Delta_{sublimation}H_m^{115}$	number of C-P		7.820161
116	$\Delta_{sublimation}H_m^{116}$	number of C-Br		5.199863

117	$\Delta_{sublimation}H_m^{117}$	number of C-I		12.0811
118	$\Delta_{sublimation}H_m^{118}$	number of N-N		8.231438
119	$\Delta_{sublimation}H_m^{119}$	number of C-A-C	A means any atom	-2.11715
120	$\Delta_{sublimation}H_m^{120}$	number of C-A-N	A means any atom	-0.41774
121	$\Delta_{sublimation}H_m^{121}$	number of C-A-O	A means any atom	-1.40174
122	$\Delta_{sublimation}H_m^{122}$	number of N-A-N	A means any atom	-1.92971
123	$\Delta_{sublimation}H_m^{123}$	number of C-A1-A2-C	A1 and A2 means any atom	1.344881
124	$\Delta_{sublimation}H_m^{124}$	number of C-A1-A2-Cl	A1 and A2 means any atom	0.696158
125	$\Delta_{sublimation}H_m^{125}$	number of Cl-A1-A2-Cl	A1 and A2 means any atom	3.321792
126	$\Delta_{sublimation}H_m^{126}$	number of C-A1-A2-A3-C	A1 , A2 and A3, means any atom	-1.13923
127	$\Delta_{sublimation}H_m^{127}$	number of C-A1-A2-A3-N	A1 , A2 and A3, means any atom	-1.49467
128	$\Delta_{sublimation}H_m^{128}$	number of C-A1-A2-A3-O	A1 , A2 and A3, means any atom	-1.02864
129	$\Delta_{sublimation}H_m^{129}$	number of C-A1-A2-A3-Cl	A1 , A2 and A3, means any atom	1.623283
130	$\Delta_{sublimation}H_m^{130}$	number of N-A1-A2-A3-S	A1 , A2 and A3, means any atom	-6.56591
131	$\Delta_{sublimation}H_m^{131}$	number of N-A1-A2-A3-Br	A1 , A2 and A3, means any atom	3.740106
132	$\Delta_{sublimation}H_m^{132}$	number of O-A1-A2-A3-S	A1 , A2 and A3, means any atom	-3.61868
133	$\Delta_{sublimation}H_m^{133}$	number of C-A1-A2-A3-A4-C	A1 , A2 , A3, and A4 means any atom	-0.26817
134	$\Delta_{sublimation}H_m^{134}$	number of C-A1-A2-A3-A4-S	A1 , A2 , A3, and A4 means any atom	3.892686
135	$\Delta_{sublimation}H_m^{135}$	number of N-A1-A2-A3-A4-N	A1 , A2 , A3, and A4 means any atom	5.043057
136	$\Delta_{sublimation}H_m^{136}$	number of N-A1-A2-A3-A4-F	A1 , A2 , A3, and A4 means any atom	-3.94056
137	$\Delta_{sublimation}H_m^{137}$	number of O-A1-A2-A3-A4-O	A1 , A2 , A3, and A4 means any atom	-0.64996
138	$\Delta_{sublimation}H_m^{138}$	number of N-A1-A2-A3-A4-A5-S	A1 , A2 , A3, A4 and A5 means any atom	-7.00242
139	$\Delta_{sublimation}H_m^{139}$	number of O-A1-A2-A3-A4-A5-F	A1 , A2 , A3, A4 and A5 means any atom	-3.71243
140	$\Delta_{sublimation}H_m^{140}$	number of C-A1-A2-A3-A4-A5-A6-Cl	A1 , A2 , A3, A4 ,A5 and A6 means any atom	-2.10959
141	$\Delta_{sublimation}H_m^{141}$	number of O-A1-A2-A3-A4-A5-A6-Cl	A1 , A2 , A3, A4 ,A5 and A6 means any atom	-4.48158
142	$\Delta_{sublimation}H_m^{142}$	number of C-A1-A2-A3-A4-A5-A6-A7-Cl	A1 , A2 , A3, A4 ,A5 ,A6 and A7 means any atom	5.212202
143	$\Delta_{sublimation}H_m^{143}$	number of N-A1-A2-A3-A4-A5-A6-A7-N	A1 , A2 , A3, A4 ,A5 ,A6 and A7 means any atom	-11.5283
144	$\Delta_{sublimation}H_m^{144}$	number of N-A1-A2-A3-A4-A5-A6-A7-O	A1 , A2 , A3, A4 ,A5 ,A6 and A7 means any atom	-10.9808

145	$\Delta_{sublimation}H_m^{145}$	number of C-A1-A2-A3-A4-A5-A6-A7-A8-C	A1 , A2 , A3, A4 ,A5 ,A6 ,A7 and A8 means any atom	-0.25142
146	$\Delta_{sublimation}H_m^{146}$	number of O-A1-A2-A3-A4-A5-A6-A7-A8-O	A1 , A2 , A3, A4 ,A5 ,A6 ,A7 and A8 means any atom	3.57817
147	$\Delta_{sublimation}H_m^{147}$	number of C-A1-A2-A3-A4-A5-A6-A7-A8-A9-N	A1 , A2 , A3, A4 ,A5 ,A6 ,A7, A8 and A9 means any atom	-19.235

R represents any group linked through carbon;

X represents any electronegative atom (O, N, S, P, Se, halogens);

Al and Ar represent aliphatic and aromatic groups, respectively;

= represents a double bond;

represents a triple bond;

-- represents an aromatic bond as in benzene or delocalized bonds such as the N-O bond in a nitro group

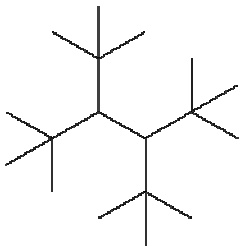
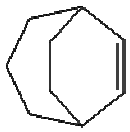
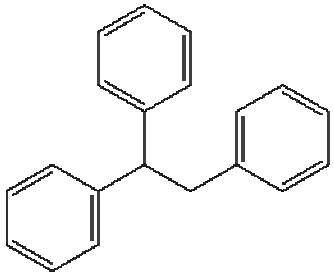
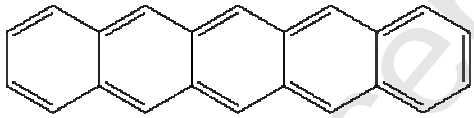
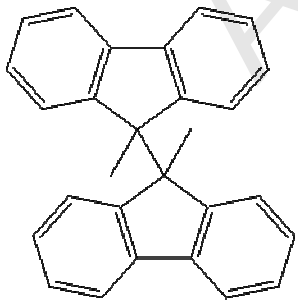
.. represents aromatic single bonds as the C-N bond in pyrrole

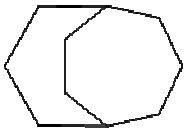
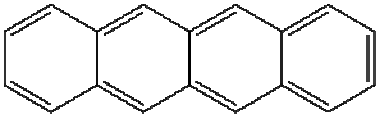
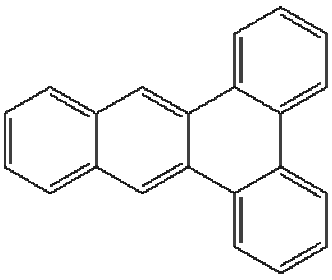
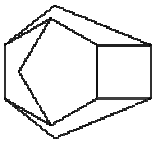
[a] The superscript represents the formal oxidation number. The formal oxidation number of a carbon atom equals the sum of the conventional bond orders with electronegative atoms; the C--N bond order in pyridine may be considered as 2 while we have one such bond and 1.5 when we have two such bonds; the C..X bond order in pyrrole or furan may be considered as 1.

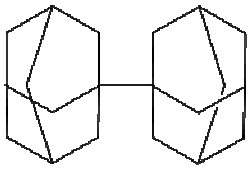
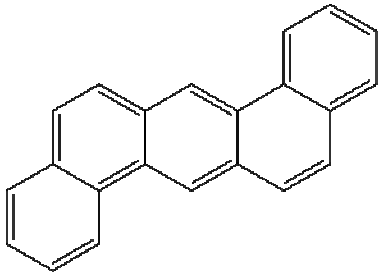
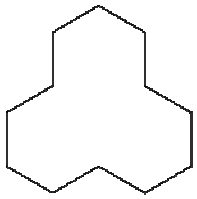
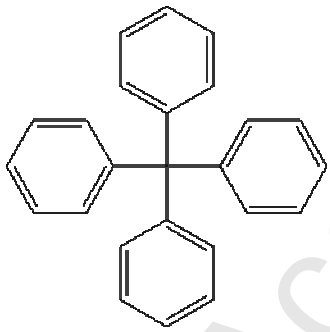
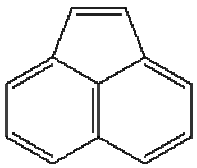
[b] As in nitro, *N*-oxides

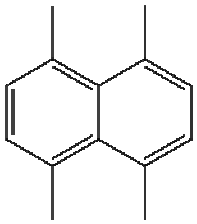
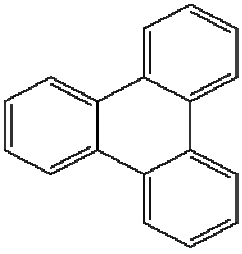
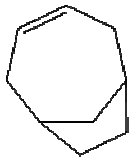
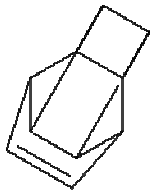
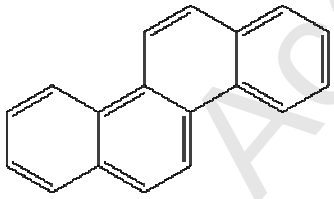
[c] Pyridine N-oxide type structure.

Table 2- Highly deviant hydrocarbons.

No.	Structure	$\Delta_{sublimation} H_m^{exp}$ / kJ.mole^{-1}	$\Delta_{sublimation} H_m^{pred}$ / kJ.mole^{-1}	%ARD
1	 1,1,2,2-tetra-tert-butylethane	74.3	40.8	45
2	 bicyclo[3.2.2]non-6-ene	48	61.2	27.5
3	 1,1,2-triphenylethane	92.2	117.2	27.1
4	 pentacene	184	137.3	25.4
5		119.7	144.5	20.8

6	9,9’-dimethyl-9,9’-bifluorenyl 	58.2	69.9	20
7	bicyclo[3.3.2]decane 	143.7	116.3	19
8	naphthacene 	159	129.9	18.3
9	dibenz[a,c]anthracene 	54.9	64.2	16.9
	Pentacyclo[5.4.0.02,6.03,10.05,9]undecane			

10		113.8	94.9	16.6
	1,1’-biadamantane			
11		162	135.4	16.4
	dibenz[a,h]anthracene			
12		76.2	63.7	16.4
	cyclododecane			
13		145.3	121.8	16.2
	tetraphenylmethane			
14		71.5	82.8	15.8
	acenaphthylene			

15		99.8	85.6	14.2
	1,4,5,8-tetramethylnaphthalene			
16		126.5	109.4	13.5
	triphenylene			
17		49.7	56.2	13.2
	bicyclo[4.2.1]non-3-ene			
18		55.3	62.5	13.1
	pentacyclo[4.4.0.02,503,804,7]dec-9-ene (basketene)			
19		131	114.4	12.6
	chrysene			

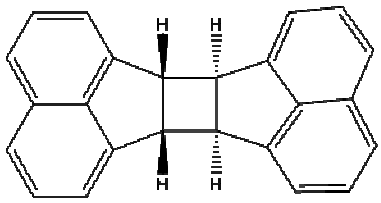
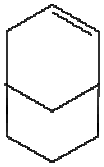
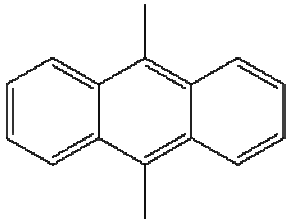
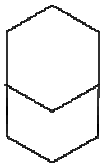
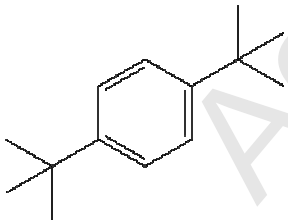
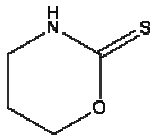
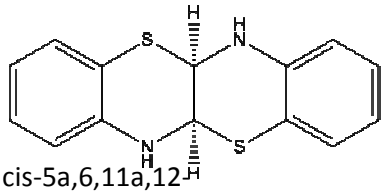
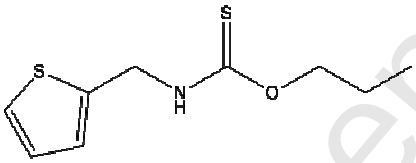
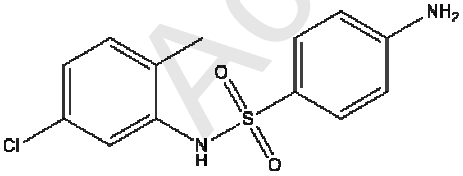
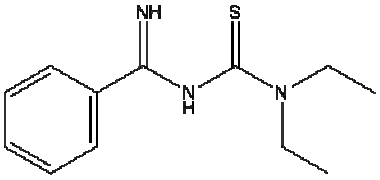
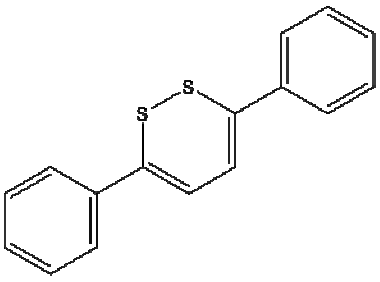
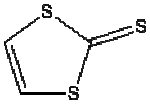
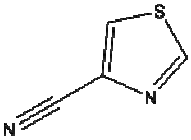
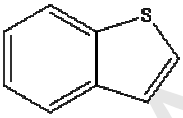
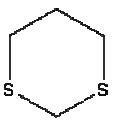
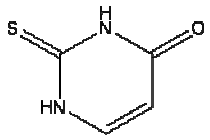
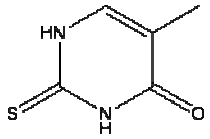
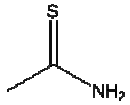
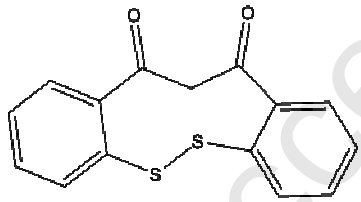
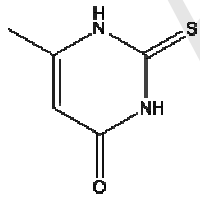
20		149	131.8	11.6
	trans-heptacyclene			
21		48.2	53.8	11.5
	bicyclo[3.3.1]non-2-ene			
22		113	100.5	11.1
	9,10-dimethylanthracene			
23		50.6	56.1	10.9
	bicyclo[3.3.1]nonane			
24		82.8	74.3	10.2
	1,4-di-tert-butylbenzene			

Table 3- Highly deviant sulfur compounds.

No.	Structure	$\Delta_{sublimation} H_m^{exp}$ / kJ.mole^{-1}	$\Delta_{sublimation} H_m^{pred}$ / kJ.mole^{-1}	%ARD
1	 tetrahydro-2H-1,3-oxazine-2-thione	108.9	80	26.6
2	 cis-5a,6,11a,12-tetrahdro[1,4]benzothiazino[3,2-b]-[1,4]-benzothiazine	123.3	149.9	21.6
3	 N-theonylthiocarbamic-O-propyl ester	136.5	110.4	19.1
4	 4-amino-N-(5-chloro-2-methylphenyl)benzenesulfonamide	130	151.7	16.7

5	 N-(diethylaminothiocarbonyl)benzamideine	126	145.8	15.7
6	 3,6-diphenyl-1,2-dithiin	183.1	155.1	15.3
7	 1,3-dithiole-2-thione	75.4	86.2	14.3
8	 4-cyanothiazole	73.9	84.2	13.9
9	 benzo[b]thiophene	65.7	74	12.6
10		61.7	69.4	12.5

11	1,3-dithiane 	138.5	121.8	12.1
12	2-thiouracil 	137.3	121.2	11.7
13	5-methyl-2-thiouracil 	83.05	73.4	11.6
14	thioacetamide 	125.5	139.9	11.5
15	monthiodibenzoylmethane 	140.7	125.9	10.5

6-methyl-2-thiouracil

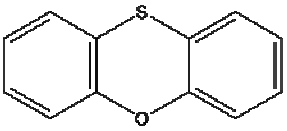
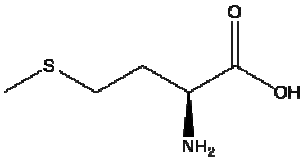
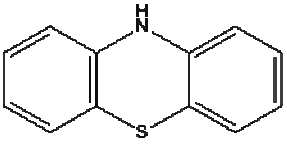
16		95.6	105.5	10.3
	phenoxathiin			
17		164	147.4	10.2
	L-(d)-methionine			
18		114.5	103.1	10
	phenothiazine			

Table 4- The deviation of the model results from experimental data for some important chemical families of the compounds.

ID	Chemical groups/families	AARD%	N
1	aliphatic esters	6.3	31
2	aromatic esters	6.4	30
3	aliphatic carboxylic acids	6.4	86
4	aromatic carboxylic acids	6.4	149
5	primary aliphatic amides	6.3	23
6	primary aromatic amides	6.5	14
7	secondary aliphatic amides	6.3	18
8	secondary aromatic amides	5.7	4
9	tertiary aliphatic amides	6.5	4
10	tertiary aromatic amides	5.5	2
11	aliphatic aldehydes	5.5	1
12	aromatic aldehydes	5	6
13	aliphatic ketones	6.3	40
14	aromatic ketones	6.3	68
15	primary aliphatic amines	6.2	20
16	primary aromatic amines	6.3	86
17	secondary aliphatic amines	6.8	17
18	secondary aromatic amines	6.5	21
19	tertiary aliphatic amines	6.5	5
20	tertiary aromatic amines	6.4	8
21	aliphatic alcohols	6.4	298
22	aromatic alcohols	6.4	156

Table 5- The comparison between the presented model and the one proposed by Ouvrard and Mitchell [16]

Chemical family	Statistical parameter	Ouvrard and Mitchell [16]	The presented model
Aliphatic hydrocarbons	*n*	33	38
	R^2	0.968	0.932
	RMSE	7.42	8.61
Aromatic hydrocarbons	*n*	50	79
	R^2	0.965	0.836
	RMSE	7	10.85
non-hydrogen bonding compounds	*n*	156	164
	R^2	0.896	0.885
	RMSE	9.98	10.56
Various compounds	*n*	226	1269
	R^2	0.925	0.826
	RMSE	9.58	10.79

Research Highlights

- A new group contribution model is presented for the estimation of sublimation enthalpy.
- A compendium of experimental data for 1271 compounds is used to develop and validate the model.
- The model shows low deviation from experimental data.