



Accurate prediction of the standard net heat of combustion from molecular structure



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ABSTRACT

A Quantitative Structure–Property Relation (QSPR) is developed to predict the standard net heat of combustion (ΔH_c°) of chemical compounds based only in their molecular structures. A Structural Group Contribution (SGC) method is used to determine ΔH_c° through two models: a Multi-Variable Regression (MVR) based on least squares and an Artificial Neural Network (ANN). The SGC method was used to probe the structural groups that have significant contribution to the overall ΔH_c° and concluded that 47 atom-type structural groups can represent the ΔH_c° for 586 pure substances. The input parameters of the SGC method are the number of occurrence of each of the 47 structural groups in each molecule. The ANN was the more accurate of the two models; it can predict ΔH_c° with an overall correlation coefficient of 0.999 and an average relative error of 0.89%. The MVR model is less accurate but is also simple and practical and provides reliable estimates. The results of both models are compared to others in the literature. The SGC method presented is very useful and convenient to assess the hazardous risks of chemicals.

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1. Introduction

The standard net heat of combustion (ΔH_c°) is defined as the increase in enthalpy when a substance in its standard state (298.15 K and 1 atm) undergoes an oxidization to produce its final combustion products: CO_2 (g), F_2 (g), Cl_2 (g), Br_2 (g), I_2 (g), SO_2 (g), N_2 (g), H_3PO_4 (s), H_2O (g) and SiO_2 (cristobalite) (AICHE, 2006). ΔH_c° , which is a measure of the energy available from a fuel, is used to compare the heating values of fuels and the stability of compounds. ΔH_c° is an important parameter when assessing the potential fire hazard of reactive chemicals and predicting the performance of explosive and propellant formulations. Knowing the exact ΔH_c° values for chemicals is essential when considering the thermal efficiency of equipment used to produce power or heat. Knowing ΔH_c° can also provide a good assessment of the environmental impact of any plant at which the complete and incomplete combustion have yet to be defined.

ΔH_c° values are compiled in databases such as AICHE-DIPPR (2006) and API-TDB (1987) for many, but not all, pure chemical compounds. These compounds are from various chemical families and can be organic or inorganic, including halogenated compounds, acids, ethers, ketones, aldehydes, alcohols, phenols, esters, amines,

anhydrides, and sulfur compounds. AICHE-DIPPR (2006) database contains approximately 2030 compounds and the list is expanding whereas API-TDB (1987) contains approximately 600 compounds. Most of these compiled ΔH_c° values are experimental, but some are calculated using the contribution method developed by Benson and coworkers (Benson and Buss, 1958). Determining ΔH_c° experimentally is tedious, expensive and sometimes impossible. When experimental ΔH_c° values are not available and determining them experimentally is inconvenient or not possible, a fast, easy, and accurate estimation method becomes necessary. Once a reliable model is obtained, it can be used to predict this property for other compounds that have not been measured or synthesized. Theoretically, the heat of combustion of transportation fuels, such as naphtha, kerosene, and diesel, can be calculated from the heat of combustion of their constituent compounds when using appropriate mixing rules and when their compositions are known. These calculations are also possible when using surrogate fuels that simulate the components of the studied fuel (Albahri, 2005a, 2005b). Therefore, knowing the ΔH_c° of the pure chemical compounds can potentially help determine the same property for undefined mixtures, such as petroleum fractions.

The experimental determination of ΔH_c° is complicated by the existence of several recognized ASTM standard test methods, which differ based on the characteristics of the studied liquid. Consequently, determining ΔH_c° experimentally is difficult, and a

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prediction method might be more convenient. For example, ASTM D240-09 (2009) is used to determine the heat of combustion of liquid hydrocarbon fuels and polymers. ΔH_c^0 is determined by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from the temperatures observed before, during, and after combustion while allowing for the appropriate thermochemical and heat transfer corrections. If a more precise method is needed, ASTM D4809-13 (2013) is used. ASTM D4868-00 (2010) is used for diesel and burner fuels while ASTM D3338/D3338M-09 (2009), ASTM D1405/D1405M-08 (2013), and ASTM D4529-01 (2011) are used for aviation fuels.

When the ΔH_c^0 of pure compounds cannot be determined experimentally, several empirical correlations in the literature can be used to determine it (Cardozo, 1986; Gharagheizi, 2008; Pan et al., 2011; Cao and Wang, 2013; Seaton and Harrison, 1990; Hshieh, 1999; Hshieh et al., 2003; Diallo et al., 2012; Wang and Li, 2000; Van Krevelen, 1990; National Technical Information Service (NTIS), 2001). Cardozo (1986) proposed a group contribution method to estimate the ΔH_c^0 for organic compounds using three simple correlations that depend on the state of the compound: solid, liquid, or gas. The input parameters are the total number of carbon atoms in the compound and the corrections for various structures and phases. The accuracy of the method was not discussed in detail, however, and the reported errors exceeded 12.5% for some compounds. Due to its simplicity, this method is useful for calculating ΔH_c^0 for complex organic compounds that are difficult to calculate using other methods.

Gharagheizi (2008) introduced a four-parameter correlation for predicting the ΔH_c^0 of pure chemicals using a Quantitative Structure–Property Relationship (QSPR) as follows:

$$\begin{aligned} \Delta H_c^0 = & -195.7155 (\pm 19.7972) - 285.9142 (\pm 3.1670) \\ & \times S_v - 162.8073 (\pm 4.6132) nC + 140.9020 (\pm 10.3094) \\ & \times \text{AST2m} + 1055.1207 (\pm 12.5430) \text{SEig} \end{aligned} \quad (1)$$

$$\begin{aligned} n_{\text{training}} = & 1372; n_{\text{test}} = 342; R^2 = 0.9954; Q_{\text{LOO}}^2 = 0.9954; Q_{\text{BOOT}}^2 \\ & = 0.9952; Q_{\text{EXT}}^2 = 0.9965; s = 5.46; a = -0.017; F \\ & = 73332.67; \Delta K = 0.111; \Delta Q = 0.000; R^P = 0.001; R^N \\ & = 0.000. \end{aligned}$$

where, ΔH_c^0 is the standard net heat of combustion, S_v is the sum of the atomic van der Waals volumes, nC is the number of carbon atoms, ATS2m is Broto-moreau autocorrelation of the topological structure, and SEig is the Eigenvalue sum from the electronegativity weighted distance matrix. Although this method is accurate ($R^2 = 0.995$), it requires additional calculations to determine the values of its intricate parameters.

Similarly, Pan et al. (2011) and Cao and Wang (2013) developed a four-parameter correlation to predict the ΔH_c^0 of pure organic compounds from their molecular structure as follows:

$$\begin{aligned} \Delta H_c^0 = & -186.755 S_v - 195.509 nC + 1110.155 \text{SEig} \\ & - 17.878 \text{SEig} - 70.391 \end{aligned} \quad (2)$$

$$n = 1322, R^2 = 0.995, Q_{\text{LOO}}^2 = 0.995, F = 64826$$

where, S_v is the sum of the atomic van der Waals volumes (scaled on carbon atom), nC is the number of carbon atoms, SEig is the eigenvalue sum from the electronegativity weighted distance

matrix, and SEig is the absolute eigenvalue sum on geometry matrix. Although these two methods are accurate ($R^2 = 0.995$ for each), similar to the method by Gharagheizi (2008), the molecular descriptors are not easy to determine.

Seaton and Harrison (1990) developed a method for calculating the ΔH_c^0 of pure compounds based on Benson's enthalpy of formation group-contribution method. Hshieh (1999) and Hshieh et al. (2003) developed simple empirical models for organosilicones and polymers. Diallo et al. (2012) developed a model for calculating the ΔH_c^0 of 53 ionic liquids using a multivariable linear regression technique where $R^2 = 0.989$. Wang and Li (2000) developed a group-bond contribution method for calculating the ΔH_c^0 of liquid alkanes that involves adding the structural group contributions and correction factors for their adjacent bonds. Van Krevelen (1990) calculated ΔH_c^0 using the heats of formation for the combustion products and reactants. This method was applied for polymeric reactants, and ΔH_c^0 was estimated from the molar contributions of the chemical groups that constitute the monomer or repeat units. The National Technical Information Service (NTIS) (2001) method calculates the standard gross heat of combustion of 66 polymers and 78 small molecules using a linear system of equations based on the structural group contributions of the molecules with an Average Absolute Error (AAE) of $\pm 2.5\%$.

For models using artificial intelligence, Gharagheizi et al. (2011) developed an accurate method for calculating the ΔH_c^0 of pure compounds from group contributions using a three layered Feed-Forward Artificial Neural Network (FFANN) model with 142 intricate structural groups as inputs where $R = 0.999$ and $\text{AAE} = 0.16\%$. Similarly, Cao et al. (2009) developed a QSPR-ANN model to predict the ΔH_c^0 for pure organic compounds using atom-type electrotopological state indices with 49 structural groups as inputs where $R = 0.992$. The model is more efficient when predicting ΔH_c^0 values below 0; consequently, the Average Absolute Deviations (AADs) for compounds containing F and Cl were very large. The experimental ΔH_c^0 value for perfluoro-*n*-pentane is 640.5 kJ/mol, while the predicted value for this compound is -413.25 kJ/mol. Therefore, the obtained deviation is 1053.75 kJ/mol with a relative error of 164.4%. The model predicts ΔH_c^0 with an AAD of 615.98 and 299.65 kJ/mol for compounds containing fluorine and chlorine, respectively (Cao et al., 2009), which is high.

Saldana et al. (Saldana et al., 2013) combined several methods to create a consensus model for predicting the ΔH_c^0 of 1624 hydrocarbon-based compounds and 1143 oxygenates (alcohols and esters) using QSPR. Various approaches were investigated from linear modeling: Genetic Function Approximation (GFA) and Partial Least Squares (PLS) to nonlinear models, such as Feed-Forward Artificial Neural Network (FFANN), General Regression Neural Networks (GRNN), Support Vector Mechanics (SVM), and Graph Machines (GM). All of the models except for the GM model use molecular descriptors and functional group count descriptors as inputs. The GM model uses SMILES formulae to define the structure of the chemical compounds used as inputs. All of the individual models have AAE of less than 2% except for the GRNN based model, which has an AAE of 4%. Therefore, Saldana et al. (2013) developed a consensus model by averaging the values computed with selected individual models to improve the generality and predictive power compared to individual predictive models. The robust consensus model, which is more accurate than each individual model alone, can predict ΔH_c^0 with $R = 0.999$, $\text{AAE} = 0.7\%$, and $\text{AAD} = 33.2$ kJ/mol. The Genetic Function Approximation Functional Group Count Descriptors (GFA-FGCD), which is the simplest of all models is expressed by the following equation:

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