Additivity methods for prediction of thermochemical properties. The Laidler method revisited. 2. Hydrocarbons including substituted cyclic compounds

Rui C. Santos [a], João P. Leal [a,b,*], José A. Martinho Simões [a,c]

[a] *Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal*
[b] *Unidade de Ciências Químicas e Radiofarmacêuticas, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal*
[c] *Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal*

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ABSTRACT

A revised parameterization of the extended Laidler method for predicting standard molar enthalpies of atomization and standard molar enthalpies of formation at $T = 298.15$ K for several families of hydrocarbons (alkanes, alkenes, alkynes, polyenes, poly-ynes, cycloalkanes, substituted cycloalkanes, cycloalkenes, substituted cycloalkenes, benzene derivatives, and bi and polyphenyls) is presented. Data for a total of 265 gas-phase and 242 liquid-phase compounds were used for the calculation of the parameters. Comparison of the experimental values with those obtained using the additive scheme led to an average absolute difference of 0.73 kJ · mol^{-1} for the gas-phase standard molar enthalpy of formation and 0.79 kJ · mol^{-1} for the liquid-phase standard molar enthalpy of formation. The database used to establish the parameters was carefully reviewed by using, whenever possible, the original publications. A worksheet to simplify the calculation of standard molar enthalpies of formation and standard molar enthalpies of atomization at $T = 298.15$ K based on the extended Laidler parameters defined in this paper is provided as supplementary material.

1. Introduction

Experimental values of standard enthalpies of formation are known for a tiny and decreasing fraction of the substances recorded by Chemical Abstracts, hindering the thermochemical assessment of many important chemical reactions. Although computational chemistry methods may afford accurate reaction enthalpies and enthalpies of formation, simple and inexpensive empirical routines will still be used at least in the next decades. Therefore, the development of more reliable procedures to predict those data is essential.

Additivity methods for estimating thermochemical properties have been widely used [1–19]. The main advantages of these methods when compared with other approaches, such as high-level theoretical calculations, is that they are simple to apply, do not require significant computing power, and usually provide very reliable values. However, the prediction of accurate data often demands a large number of empirical "parameters", which in turn require many experimental values of the property to be parameterized. This is indeed the major disadvantage of additivity methods: their

empirical nature requires a reliable (experimental and/or computational) data collection.

In a previous paper one of us introduced an extended version of the Laidler method and applied it to a large number of hydrocarbons, stating also the intention to cover other families of compounds in future publications [17]. Most, but not all, of the work done relied on several databases, mainly Pedley's compilation [13]. However, it was found later that some values from that database and also from NIST Chemistry WebBook [20] were not properly assigned. It was therefore decided to evaluate, whenever possible, all the experimental values, based on the original papers. On the other hand, a substantial increase in the database allowed calculating additional parameters, particularly for cyclic compounds. Also, some parameters were redefined and new ones added, including more non-bonded interactions, which allowed coverage of rather bulky compounds. Finally, in cases where conflicting experimental data exist, high-level theoretical calculations were performed to clarify the situation, *i.e.* to help selecting the "best" experimental value.

The results of this evaluation work, which are reported in the present paper, pave the ground to extend the model to other families of molecules, including compounds with heteroatoms.

The standard molar enthalpy of formation $(\Delta_f H_m^\circ)$ is a key property because it reflects the enthalpic content of a molecule. It also allows calculating the enthalpy of any reaction where that molecule is involved, provided that the enthalpies of formation of all

* Corresponding author. Address: Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal. Tel.: +351 219946219.

E-mail addresses: jpleal@fc.ul.pt, jpleal@itn.pt (J.P. Leal).