VERIFICATION OF THE ENTHALPIES OF FORMATION OF ORGANIC COMPOUNDS: A REFINEMENT STRATEGY BASED ON QUANTUM CHEMICAL CALCULATIONS

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Prediction and verification of thermochemical properties are central to assessing the feasibility, selectivity, and efficiency of chemical processes. In industrial practice, the majority of transformations occur in the liquid phase, making standard enthalpies of formation and entropies in the condensed state key parameters for reliable thermodynamic modeling. However, for complex and multifunctional organic compounds, the availability of consistent and experimentally validated data remains limited, which significantly constrains accurate process design.

Traditional estimation methods, such as group additivity approaches and structure–property correlations, often fail to provide sufficient accuracy for condensed systems and require extensive calibration against reliable datasets. At the same time, quantum chemical thermochemistry offers significant predictive capabilities, but widely used approaches – atomization methods and well balanced reaction schemes – suffer from systematic errors, dependence on reference compounds, and methodological ambiguity in reaction selection.

To address these challenges, a hybrid GAQCC (Group Additivity with Quantum Chemical Calibration) approach is proposed for the calculation and verification of gas-phase standard enthalpies of formation. The method is based on decomposition of molecular energy into two contributions: an additive term associated with transferable structural fragments and a non-additive term reflecting specific intramolecular effects, including conjugation, steric strain, and electronic interactions.

In contrast to conventional group contribution methods, the additive parameters are not purely empirical but are calibrated using high-level quantum chemical calculations (G3MP2) in combination with critically evaluated experimental thermochemical data. The quantum chemical calculations are primarily used to determine the non-additive contribution, which is significantly smaller than the total molecular energy and therefore less sensitive to residual methodological errors.

The proposed approach eliminates the need for constructing balanced reaction schemes, reduces systematic uncertainties, and ensures internal consistency of the results. As a consequence, GAQCC provides a robust and reproducible framework for validation, refinement, and extension of thermochemical databases, enabling more reliable thermodynamic analysis and design of chemical processes.

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