ASSURE X23 Project: Revision of the Benchmark for Sublimation Enthalpy Calculations

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Molecular crystals are ubiquitous. They play a role in practically every sector of industry and human activity in general. The field of experimental thermodynamics cannot keep up with the growth rate of newly synthesized chemicals, not even those that are industrially interesting. Computational chemistry, on the other hand, offers high capacity for screening of materials with promising properties. The possibilities of computational chemistry evolve rapidly and state-of-the-art reference data are required for benchmarking of the newly developed and refined methods.

The C21 database (Otero-de-la-Roza and Johnson, 2012) and its extended version X23 (Reilly and Tkatchenko, 2013, Dolgonos et al., 2019) are widely used reference datasets for quantum-chemical calculations of sublimation enthalpies of molecular materials. They contain information on crystal structures, their corresponding experimental sublimation enthalpies, and corrections between the sublimation energy and the lattice energy. Despite being widely used, it should be questioned whether these datasets represent state-of-the-art reference data or whether they should be revised. The aim of this project is to integrate experimental thermodynamics, computational, and crystallographic efforts in order to Analyze, Supplement, Substitute, Unite, Rectify, and Endorse (ASSURE) the X23 reference dataset to reduce its uncertainty towards the current limits.

In this contribution, the first step of the project will be discussed: detailed analysis of the C21 and X23 reference data and their uncertainties. The overall uncertainty of the reference values will be estimated based on the uncertainty of the respective experiments taken from the primary literature, statistical treatment, additional uncertainties due to experimental complications, non-ideal behavior, polymorphism, and other sources that were neglected so far. Compounds eligible for experimental re-examination and those for replacement in the revised dataset will be suggested.

In further work, new experimental data will be collected for selected X23 compounds at the state-of-the-art level, namely vapor pressures, heat capacities, and phase behavior properties. Different techniques will be combined to minimize the uncertainty of the derived sublimation enthalpy values including enforcing consistency with properties of the liquid phase. In addition, the correction terms required to obtain sublimation enthalpy at 0 K and back-corrected lattice energies will be revised, including an assessment of their uncertainties targeting the convergence of the lattice energy to the sub-kJ/mol accuracy. The experimental work on the first group of compounds, nitrogen heterocycles (imidazole, s-triazine, pyrazine, and pyrazole), will be presented in a poster contribution (ID 134).

References

1. Otero-de-la-Roza, A.; Johnson, E. R., A benchmark for non-covalent interactions in solids. *J. Chem. Phys.* **2012,** 137, (5), 054103.
2. Reilly, A. M.; Tkatchenko, A., Understanding the role of vibrations, exact exchange, and many-body van der Waals interactions in the cohesive properties of molecular crystals. *J. Chem. Phys.* **2013,** 139, (2), 024705.
3. Dolgonos, G. A.; Hoja, J.; Boese, A. D., Revised values for the X23 benchmark set of molecular crystals. *Phys. Chem. Chem. Phys.* **2019,** 21, (44), 24333-24344.