ASSURE X23 Project: Reconciliation of Experimental Data for Heterocyclic Compounds

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This contribution follows oral (ID 133), where the concept of the ASSURE X23 project is presented. Its aim is to integrate experimental thermodynamics, computational, and crystallographic efforts in order to Analyze, Supplement, Substitute, Unite, Rectify, and Endorse (ASSURE) the X23 reference dataset (Otero-de-la-Roza and Johnson, 2012, Reilly and Tkatchenko, 2013, Dolgonos, et al., 2019) to reduce its uncertainty towards the current limits.

Having the uncertainties of the C21 and X23 reference data analyzed, re-investigation of selected X23 compounds was initiated. The experimental work on the first set of compounds, nitrogen heterocycles (imidazole, s-triazine, pyrazine, and pyrazole), is presented. These compounds are small hygroscopic molecules, which range from medium to low volatility. With their properties, determination of the sublimation enthalpy calorimetrically or through vapor pressure measurements should be quite accurate, but it might appear problematic to prepare a dry and pure sample. The number of literature sources is small (only 2 to 4), and although they agree relatively well, all but one are dated before 1990. At least s-triazine and pyrazine are polymorphic, which was not taken into consideration during the development of the X23 reference values.

Simultaneous correlation of vapor pressures and related thermal properties, SimCor (Růžička and Majer, 1994) represents an effective way for development of reliable and thermodynamically consistent sublimation enthalpies. Several thermodynamically bound properties are treated simultaneously: vapour/sublimation pressures, vaporization/sublimation enthalpies, and differences in heat capacities. Properties of the liquid and crystal can be also correlated together with the fusion enthalpy and melting temperature. SimCor is based on exact thermodynamic relationships and therefore care must only be given to reliability of the input data.

Vapor pressures and crystal heat capacities were re-examined over a wide temperature range including near room temperature. Phase behavior and crystal structures were studied by differential scanning calorimetry and X-ray powder diffraction to exclude any ambiguity in the phase to which the properties correspond. The experimental data were joined with ideal-gas properties calculated by statistical thermodynamics and literature values in order to develop new, more reliable sublimation enthalpy reference values using the SimCor method. Differences from the previous recommendation and uncertainties of both values are discussed.

References

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