Extensive Study of Sublimation Behavior of Amino Acids

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Amino acids are compounds with unique zwitterionic structure providing a high cohesive energy density, which together with their limited thermal stability, strongly restricts their study in the crystalline phase. Despite their biological role, sublimation thermodynamic properties are reported only for nine of the proteinogenic amino acids (PAAs), generally in a short temperature range and without a possibility of interlaboratory comparison. Considering the availability of experimental thermodynamic data and demands on their determination, the method of simultaneous correlation is the only approach for determination of sublimation behavior of PAAs at the temperatures of interest (typically 0 K and 298.15 K). To the employment of simultaneous correlation method must however precede a new determination of vapor pressures and related properties with the lowest uncertainty available nowadays. A new Knudsen effusion apparatus with a quartz crystal microbalance was developed and used for measurement of vapor pressures of a series of PAAs. Some details on optimization of experimental methodology for the specifics of PAAs studied will be presented. Heat capacities of the crystalline phase were measured applying three types of calorimeters/methodologies: PPMS, Tian-Calvet, and DSC to obtain a reliable description over the entire range from 0 K to temperature region of the vapor pressure measurements. Special attention was devoted to study of polymorphic behavior. Ideal-gas thermodynamic properties were calculated using a combination of quantum chemical calculations and the statistical thermodynamics model R1SM with focus on conformational space of the molecules and uncertainty of their relative energies. A complex and systematic study of (solid-)solid-vapor equilibria of PAAs will contribute to the understanding of stability of molecular crystals. The outcomes of this study can be used as reference data for verification of theoretical models for calculation of Gibbs energies of crystalline forms (a parallel project).

The authors acknowledge financial support from the Czech Science Foundation (GACR no. 17-03875S).