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Solution calorimetry as a complementary tool for the determination of enthalpies of vaporization and sublimation of low volatile compounds at 298.15 K

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ABSTRACT

In this work a new solution-based calorimetry approach for determination of the sublimation and vaporization enthalpies of low volatile compounds was proposed. The approach is based on the measurement of solution enthalpy of a molecule of interest in benzene and as well as the measurement of molar refraction index for this molecule. Enthalpies of solution at infinite dilution in benzene for a set of 18 aromatic and polyaromatic hydrocarbons were measured at 298.15 K. Experimental data on vaporization/sublimation enthalpies for this set were collected from the literature. For validation of the literature data additional sublimation experiments were performed for phenanthrene, 1-phenylnaphthalene, 1,2-diphenylbenzene, 1,2,3,4-tetraphenylnaphthalene, hexaphenylbenzene, and rubrene using transpiration, quartz crystal microbalance, and thermogravimetry. Vaporization/sublimation enthalpies derived from the solution calorimetry approach were in good agreement (within experimental uncertainties) with those measured by conventional methods. The solution-based calorimetry approach gives a reliable and quick appraisal of vaporization/sublimation enthalpies. This approach constitutes a complementary additional thermochemical option for vaporization/sublimation enthalpies data evaluation as well as for rapid data gathering for low volatile and/or thermally unstable organic compounds.

Introduction

Energetics of vaporization and sublimation processes impairs industrial phase separation operations. It governs solubility in pharmaceuticals or volatilization of chemicals from soil. Enthalpies of vaporization/sublimation are also required to obtain energetics of molecules and chemical reactions in the gas state, and in this context the knowledge of vaporization/sublimation enthalpies is indispensable (in combination with classic combustion calorimetry) for validation of the modern high-level quantum chemical calculations [1]. During the last two centuries, a large number of direct (calorimetric) and indirect (from vapor pressure temperature dependences) experimental methods have been developed to obtain vaporization/sublimation enthalpies [2]. Yet, most of the available methods are only sufficiently developed for measurements of highly volatile and volatile compounds. As a rule, the available vaporization enthalpies of these compounds are consistent. The discrepancies sometimes observed among the data are typically due to possible impurities in the sample under study. In contrast, only few experimental methods are well established for the low volatile compounds: the mass effusion Knudsen method (ME), the quartz crystal microbalance (QCM), the transpiration method, and thermogravimetric analysis (TGA) [2]. The latter methods are less affected by possible impurities because of the careful preconditioning of the sample in the measuring unit prior to beginning of the experiment. However, it should be noticed, that the quality of results from these four methods is crucially dependent on operator competency and experience. Conventionally, for the sake of comparison, the measured vaporization/sublimation enthalpies are reported in original works or compilations at the reference temperature 298.15 K. The highly

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