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Thermochemical properties of mono- and di-cyano-aromatic compounds at 298.15 K

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ABSTRACT

The solution calorimetry approach was applied for the determination of the sublimation enthalpies for cyano-aromatic compounds. According to this approach, the vaporization/sublimation enthalpies were estimated as a difference between solution (cr/l to the solution) and solvation (gas to the solution) enthalpies in acetonitrile as a solvent. The solvation enthalpy of studied compounds was calculated using the previously developed and tested additive scheme. The solution enthalpies of five cyano-aromatic compounds were measured experimentally for the first time by using solution calorimeter.

The new approach for the evaluation of the condensed state enthalpy of formation by using first principles calculations and solution calorimetry technique is proposed. In most cases obtained results are in good agreement with literature values.

Apparatus for determination of vapor pressure by using the transpiration method was developed. The experimental setup was tested by measuring the vapor pressure of pure naphthalene. Vapor pressures for 1- and 2-cyano-naphthalenes were measured by using the newly elaborated transpiration setup. Experimental and calculated values of sublimation enthalpies are in good agreements with the most reliable available literature data. Sublimation enthalpy of 9-cyano-anthracene was obtained by solution calorimetry for the first time.

1. Introduction

The thermochemical parameters of phase changes are among the most important characteristics of pure substances and materials. The thermochemical data on phase transitions play a key role in the evaluation of the gas-liquid equilibrium needed to design a purification apparatus [1]. Moreover, the enthalpies of phase transitions, in particular, the enthalpy of fusion are an indispensable part of evaluation and simulation of the dependence of the solubility of the compound by the temperature [2,3]. A solubility diagram can be presented as a superposition of solubility temperature dependence curves for each component of a binary system by using the Shreder-Le Châtelier equation [1].

Thermodynamic properties of the cyano-aromatic compounds are poorly presented in the literature [4–6]. For example, the thermochemical data on the enthalpies of vaporization and sublimation of poly-cyano-benzenes, naphthalenes and anthracenes are absent in the literature. A better situation is observed for the sublimation enthalpies of *di*-cyano-benzenes and mono-cyano-naphthalenes. These compounds were studied by using various methods [4–6]. *Di*-cyano-benzenes were studied by gas saturation method [4,5]. The values of sublimation enthalpies of 1- and 2-cyano-naphthalenes were determined by high-temperature Calvet microcalorimetry and Knudsen effusion technique [6]. However, for most of the considered compounds only single determination can be found. In such case, any further analysis will be very tricky, while possible errors cannot be eliminated by comparison of the results of different techniques.

Recently, it was shown that the enthalpies of vaporization/sublimation at 298.15 K can be derived using the solution calorimetry (SC) method [7,8]. The important advantage of the SC method is that vaporization/sublimation enthalpies are evaluated directly at 298 K. It is due to the fact that solvation and solution enthalpies used for determination vaporization and sublimation enthalpies are determined at 298.15 K. Due to this reason the SC method can be used for studies of thermally unstable and explosive compounds. Another advantage of the SC technique comes from the well-known fact, that the application of the conventional methods for determination of phase transition enthalpies of low volatile compounds is not a trivial task [8]. At the same time, the SC method was already successfully applied for low volatile

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