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# Enthalpies of solution, enthalpies of fusion and enthalpies of solvation of polyaromatic hydrocarbons: Instruments for determination of sublimation enthalpy at 298.15 K

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**A R T I C L E   I N F O**

**A B S T R A C T**

In this work a simple method for calculation of solvation enthalpies of polyaromatic hydrocarbons (PAHs) in various solvents at 298.15 K was proposed. According to this method the enthalpy of solvation of a polyaromatic hydrocarbon in a particular solvent can be calculated on the basis of the general formula of the compound, the solvation enthalpy of benzene in the same solvent and parameter related to the contribution of hydrogen atom into solvation enthalpy. The validity of the proposed method was confirmed by the comparison of calculated and experimentally measured values of solvation enthalpies of PAHs in benzene, tetrahydrofuran and acetonitrile. This method was used for determination of the sublimation enthalpy of PAHs at 298.15 K based on the general relationship between the enthalpy of sublimation/vaporization of the compound of interest and its enthalpies of solution and solvation in the same solvent at 298.15 K. Enthalpies of solution at infinite dilution of several PAHs were measured in acetonitrile, benzene and tetrahydrofuran at 298.15 K. It was shown that solution enthalpies of PAHs in benzene at 298.15 K are approximately equal to their fusion enthalpies at the melting temperature. Solvation enthalpies of 15 PAHs at 298.15 K calculated according to the proposed method together with corresponding fusion enthalpy values (at the melting temperature) were used to calculate the sublimation enthalpy values at 298.15 K. Comparison of the obtained results with recommended values of sublimation enthalpy shows that fusion enthalpies at the melting temperature can be used instead of the solution enthalpies in benzene at 298.15 K for calculation of the sublimation enthalpy at 298.15 K.

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## 1.  Introduction.

Many polyaromatic hydrocarbons (PAHs) possess carcinogenic properties. Significant amount of PAHs are entering the environment via high-temperature processes in chemical and petrochemical industries. Because of this, the research on thermodynamics of phase transitions of PAHs is a topic of constant interest. A number of studies on this problem were reported earlier [1–6]. Most comprehensive collections of data on enthalpies of vaporization and sublimation of PAHs are presented in [1,2,7].

A large number of methods for determining the enthalpy of vaporization and sublimation exist. All of them are based on different fundamental principles and have some strong and weak sides, which were discussed earlier [8]. In previous works [1,9–11] we

developed an approach for experimental determination of liquid-vapor and solid-vapor phase transition enthalpies using solution calorimetry technique at 298.15 K. It is based on the general relationship between the enthalpy of sublimation/vaporization of the compound of interest and its enthalpies of solution and solvation in the same solvent at 298.15 K. Enthalpy of solvation is calculated based on the linear correlation between molar refraction (determined from the experimental data of density and refractive index) and enthalpy of solvation [1,9,10,12,13] or using additive scheme [11]. Enthalpy of solution is measured experimentally by direct solution calorimetry technique. This approach has some advantages. First, results are derived directly at the reference temperature 298.15 K (ambiguous temperature adjustment is not required) without transfer of molecule of interest to the gas phase. Second, it can be applied for studies of thermally unstable and/or explosive compounds. Third, solution calorimetry measurements are quick and less demanding as compared to conventional methods. In recent work [1], we applied this approach to

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