# 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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A B S T R A C T

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-phenyl-naphthalene, 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.

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## 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

volatile and volatile compounds are easily measured by calorimetric methods directly at 298.15 K. Measurements of low volatile compounds require increasing of temperature of about 100–200 K above the $T = 298.15$ K. The Kirchhoff's equation is used for the temperature adjustment of vaporization/sublimation enthalpies from $T_{av}$ (average temperature of the experimental range) to $T = 298.15$ K. Heat capacity differences required for the Kirchhoff's equation are usually derived from empirical correlations. One of the most frequently used procedures was suggested by Chickos et al. [3]. This method was parameterized using the data set of the gaseous heat capacities restricted to small volatile molecules because experimental heat capacities for large molecules are absent. Due to this fact using of the Kirchhoff's equation for adjustment from $T_{av}$ to the reference temperature $T = 298.15$ K may be possibly uncertain, especially when the vaporization experiment was performed at $T_{av}$ lying by 100–200 K above 298.15 K [4].

Summing up, results from conventional experimental methods for measurement of vaporization/sublimation enthalpies are sensitive to possible impurities, operator experience, and ambiguity of the temperature adjustment to 298.15 K. Each of these factors could affect, in different extents, the reliability of the vaporization/sublimation enthalpies reported in the literature. Thus, a careful evaluation of the experimental data with the recommendation of the reliable enthalpies including their uncertainties is a highly valuable work [5,6]. In this respect, any additional independent method to assess vaporization/sublimation enthalpies could be very helpful to resolve contradictions in the data available in the literature. For example, the available sublimation enthalpies of 9,9′-bianthracene 128.4 kJ mol$^{-1}$ [7] and 148.1 kJ mol$^{-1}$ [8] are different by nearly 20 kJ mol$^{-1}$. Both values were measured with well established methods in thermochemical research labs with sufficient experiences. However, it is hardly possible to determine the preferred value without an additional study. Also, very often only a single value can be found in the literature, e.g. the sublimation enthalpy 178.2 kJ mol$^{-1}$ of 5,6,11,12-tetraphenylnaphthacene (rubrene) was measured by using the ME method [7]. Thus, another method is required to prove validity of this value.

Some time ago we have revealed [9,10], that the solution calorimetry measurements at 298.15 K could provide an additional method to assess vaporization/sublimation enthalpies especially for large compounds. The solution calorimetry approach utilizes an empirical correlation of the solvation enthalpy of a molecule of interest with its molar refraction. For example, the sublimation enthalpy of biphenyl available in the literature was measured using five different methods with values spreading from 81 to 84 kJ mol$^{-1}$, with an average value of $(82.1 \pm 2.1)$ kJ mol$^{-1}$ recommended in Ref. [5]. The value of $(82.8 \pm 1.5)$ kJ mol$^{-1}$ derived from the enthalpy of solution of biphenyl in cyclohexane in our preliminary study [10] is in fair agreement with the recommendation. Thus, the solution calorimetry seems to be a promising tool for evaluation of vaporization/sublimation enthalpy data. The main goal of this work was to establish a reliable approach based on the results from solution calorimetry. There are at least three crucial advantages in the utilization of solution calorimetry. First, this method is already well established in physical chemistry classes. Second, inexpensive commercial devices are used. Third, experiments are performed directly at the reference temperature (298.15 K) favorably overcoming the temperature adjustment limitations inherent in vapor pressure measurements.

In this work we have been challenged to develop and apply the solution calorimetry approach to derive vaporization/sublimation enthalpies for a number of aromatic and polyaromatic hydrocarbons, where the experimental data according to recent compilation [5] seem to be in disarray. For validation of the results from solution calorimetry we additionally used the well established transpiration, QCM, and TGA methods.

## 2. Experimental part

### 2.1. Materials

All aromatic hydrocarbons studied in this work were of commercial origin with mass fraction purities >0.97. They were further purified by repeated crystallization or by fractional sublimation in vacuum. Purities of aromatic hydrocarbons were analyzed by using the Konik 5000 gas chromatograph (GC) equipped with a flame ionization detector (FID). Some samples were analyzed using simultaneous TGA and differential scanning calorimetry (DSC) (Thermoanalyzer Netzsch STA 449C Jupiter) coupled with evolved gas analysis by mass spectrometry (quadrupole mass-spectrometer QMS 403C Aeolos).

The calorimetric solvent, benzene, was carefully purified from traces of thiophene by shaking with the concentrated $H_2SO_4$. Then it was washed with the dilute aq. NaOH and water and then distilled over $CaH_2$. The mass fraction of benzene after purification was 0.999 according to GC analysis.

Water used for calibration of solution calorimetry, densimetry and refractometry techniques was distilled twice and deionized using the purification system Easy Pure II (Thermo Scientific). Its electrical resistivity was 18.2 M$\Omega$ cm.

### 2.2. Solution calorimetry

Enthalpies of solution of aromatic hydrocarbons in benzene were measured at $T = 298.15 \pm 0.01$ K using the commercial TAM III solution calorimeter. In a typical experiment, 100 mL of benzene were placed in a glass calorimetric cell equipped with a gold stirrer, a Joule heater, and a thermistor. The detailed description of the standard solution procedure has been published elsewhere [11,12].

#### 2.2.1. Liquid samples

Dissolution experiments with liquid samples were performed by using the titration procedure: 100 μL of solute were dropped into the thermostatted cell in small portions of 10–20 μL with help of an electronically operated microliter syringe equipped with a long gold cannula with the tip immersed in the measuring cell. The heat effect of each addition was calculated from a calorimetric curve. Experimental and data acquisition procedures were tested by measuring the solution enthalpy of propan-1-ol in water. The average value of the solution enthalpy of $(-10.16 \pm 0.03)$ kJ mol$^{-1}$ determined across 5 experiments was in excellent agreement with the recommended value $(-10.16 \pm 0.02)$ kJ mol$^{-1}$ [13].

#### 2.2.2. Solid samples

Dissolution of solid samples was carried out using the ampoule technique. A cylindrical glass ampoule was filled with the sample (0.01–0.05 g), sealed, weighed ($\pm 0.01$ mg), inserted in the sample holder, and immersed into the solvent. After thermal equilibration with the solvent the ampoule was broken and the temperature change in the cell was registered. Each solid sample was measured at least 4 times. Experimental and data acquisition procedures were tested by dissolution of KCl in water. The average value of the solution enthalpy of $(17.41 \pm 0.04)$ kJ mol$^{-1}$ measured across 5 experiments was in excellent agreement with the recommended value $(17.47 \pm 0.07)$ kJ mol$^{-1}$ [14].

All experimental enthalpies of solution for aromatic hydrocarbons in benzene measured in this work are listed in Table S1. Analysis of the measured values did not reveal any concentration dependence of solution enthalpies within the boundaries of their uncertainties. This fact proved the assumption that a solute ($A_i$) dissolves in sufficient amount of solvent ($S$) to give a solution of infinite dilution. Average values of solution enthalpies of aromatic hydrocarbons in benzene obtained from at least 4 measurements

**Table 1**

Enthalpies of solution in benzene, $\Delta_{soln}H^{A_i/C_6H_6}$, molar refractions, $MR^{A_i}$, enthalpies of solvation, $\Delta_{solv}H^{A_i/C_6H_6}$, used for calculation of enthalpies of sublimation, $\Delta_{cr}^g H_m^{A_i}$, of aromatic hydrocarbons with Eq. (8) or (9) (all values at 298.15 K; uncertainties are expressed as standard deviation).

| Compound ($A_i$) | $\Delta_{soln}H^{A_i/C_6H_6}$ [a] (kJ mol$^{-1}$) | $MR^{A_i}$ (cm$^3$ mol$^{-1}$) | $\Delta_{solv}H^{A_i/C_6H_6}$ (kJ mol$^{-1}$) | $\Delta_{cr}^g H_m^{A_i}$ (Eq. (9)) (kJ mol$^{-1}$) | $\Delta_{cr}^g H_m^{A_i}$ (Table 3) [d] (kJ mol$^{-1}$) | $\Delta$ [e] (kJ mol$^{-1}$ (%)) |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Azulene (cr) | 18.1 ± 0.2 | 44.4 ± 0.5 | −55.2 | 73.3 ± 0.7 | 74.2 ± 2.2 | 0.9 (1.3) |
| Diphenylacetylene (cr) | 18.2 ± 0.1 | 62.0 ± 0.9 [b] | −74.3 | 92.5 ± 1.0 | 91.9 ± 3.2 | −0.6 (0.7) |
| Phenanthrene (cr) | 17.7 ± 0.1 | 62.3 ± 0.6 | −74.6 | 92.3 ± 1.1 | 92.1 ± 0.6 | −0.2 (0.3) |
| trans-Stilbene (cr) | 24.9 ± 0.2 | 65.3 ± 0.7 | −77.9 | 102.8 ± 0.9 | 101.7 ± 1.2 | −1.1 (1.1) |
| 1-Phenylnaphthalene (l) | 0.7 ± 0.1 | 69.1 ± 0.7 | −82.0 | 82.7 ± 0.8 [c] | 81.9 ± 1.0 [c] | −0.8 (1.0) |
| Fluoranthene (cr) | 18.1 ± 0.2 | 71.5 ± 0.7 | −84.7 | 102.8 ± 0.9 | 100.5 ± 1.4 | −2.3 (2.2) |
| Pyrene (cr) | 16.3 ± 0.2 | 74.1 ± 0.7 | −87.5 | 103.8 ± 0.9 | 99.3 ± 1.8 | −4.5 (4.5) |
| 1,2-Diphenylbenzene (cr) | 15.2 ± 0.2 (14.87 ± 0.03) [f] | 76.9 ± 0.8 | −90.5 | 105.7 ± 1.0 | 103.0 ± 1.4 | −2.7 (2.6) |
| 1,3-Diphenylbenzene (cr) | 22.3 ± 0.1 (21.92 ± 0.03) [f] | 79.4 ± 0.1 [b] | −93.2 | 115.5 ± 0.2 | 118.2 ± 1.4 | 2.7 (2.2) |
| 1,4-Diphenylbenzene (cr) | 27.5 ± 0.4 (27.41 ± 0.28) [f] | 79.9 ± 0.8 | −93.8 | 121.3 ± 1.2 | 123.8 ± 1.2 | 2.5 (2.0) |
| 1,2-Benzanthracene (cr) | 19.1 ± 0.1 | 82.9 ± 0.8 | −97.1 | 116.2 ± 0.9 | 116.2 ± 0.6 | 0.0 (0.0) |
| 9-Phenylanthracene (cr) | 21.6 ± 0.2 | 89.2 ± 0.2 [b] | −103.9 | 125.5 ± 0.4 | 120.3 ± 0.8 | −5.2 (4.3) |
| 1,2,3-Triphenylbenzene (cr) | 20.2 ± 0.5 | 102.5 ± 0.2 [b] | −118.4 | 138.6 ± 0.7 | 136.8 ± 0.8 | −1.8 (1.3) |
| 1,2,5,6-Dibenzanthracene (cr) | 28.1 ± 0.5 | 104.2 ± 1.0 | −120.2 | 148.3 ± 1.5 | 148.5 ± 1.0 | 0.2 (0.1) |
| 9,10-Diphenylanthracene (cr) | 18.7 ± 0.4 | 117.0 ± 0.6 [b] | −134.2 | 152.9 ± 1.0 | 153.6 ± 0.8 | 0.7 (0.5) |
| 1,2,3,4-Tetraphenylnaphthalene (cr) | 4.0 ± 0.5 | 141.5 ± 1.1 [b] | −160.8 | 164.8 ± 1.6 | 160.2 ± 1.6 | −4.6 (2.9) |
| Hexaphenylbenzene (cr) | 2.6 ± 0.5 | 171.4 ± 1.7 | −193.3 | 195.9 ± 2.2 | 196.6 ± 1.0 | 0.7 (0.3) |
| Rubrene (cr) | 10.6 ± 0.2 | 179.9 ± 1.8 | −202.6 | 213.2 ± 2.0 | 213.9 ± 1.3 | 0.7 (0.3) |

[a] Measured in this work.
[b] Measured in this work (see Table S2).
[c] Enthalpy of vaporization, $\Delta_l^g H_m^{A_i}$.
[d] Recommended and selected values from Table 3.
[e] Difference between column 6 and 5.
[f] Measured in Ref. [15].

are presented in Table 1. Solution enthalpies of terphenyls in benzene measured in this work are in excellent agreement with the data obtained by Ogawa and Sugiura [15] which serves as an additional confirmation of data reliability.

### 2.3. Molar refraction

Values of molar refraction of aromatic hydrocarbons ($MR^{A_i}$) in benzene solutions at 298.15 K were derived from experimental refractive indices and densities according to Eq. (1).

$$MR^{A_i} = \frac{1}{x_2}\left[\frac{n_{12}^2 - 1}{n_{12}^2 + 2} \times \frac{M_{A_i}x_2 + M_{Bz}(1-x_2)}{d_{12}} - MR^{Bz} \times (1-x_2)\right] \quad (1)$$

where $MR^{A_i}$ is the molar refraction of an aromatic hydrocarbon; $x_2$ is the mole fraction of aromatic hydrocarbon in benzene solutions; $M_{Bz}$ and $M_{A_i}$ are the molar masses of benzene and an aromatic compound; $d_{1,2}$ is the density of the benzene solution of an aromatic hydrocarbon with the mole fraction $x_2$; $n_{12}$ is the refractive index of solutions of aromatic hydrocarbon in benzene; $MR^{Bz}$ is the molar refraction of benzene, which was calculated by Eq. (2) using experimental data.

$$MR^{Bz} = \frac{M_{Bz}}{d_{Bz}}\frac{n_{Bz}^2 - 1}{n_{Bz}^2 + 2}, \quad (2)$$

where $M_{Bz}$ is the molar mass of benzene; $d_{Bz}$ is the experimental density of benzene; and $n_{Bz}$ is the experimentally measured refractive index of benzene. All auxiliary data were measured at 298.15 K. Obtained molar refractions of 6 aromatic hydrocarbons are presented in Table 1.

### 2.4. Auxiliary quantities

Refractive indices required for calculation according to Eq. (1) were measured at 298.15 ± 0.01 K by using the automatic digital refractometer RX-5000 alpha (Atago Co., Ltd.). Accuracy and repeatability of this instrument are 0.00004 and 0.00002,

respectively. The refractometer was calibrated with water. Experimental refractive indices of aromatic hydrocarbons are collected in Supporting Material (Table S2).

Densities of neat liquids as well as densities of solutions, $d_{1,2}$, required for calculation of the molar refraction in Eq. (1) were measured by a vibrating-tube densimeter Anton Paar DSA 5000 M with an accuracy of 0.000005 g cm$^{-3}$ and repeatability of 0.000001 g cm$^{-3}$. The densimeter was calibrated with water and air following the instructions and requirements of the manufacturer. Calibrations and all measurements were performed at temperature 298.15 ± 0.01 K. The auxiliary data are presented in Supporting Material (Table S2).

### 2.5. Transpiration method: vaporization or sublimation enthalpy measurements

Vapor pressures over the liquid 1-phenylnaphthalene, 1,2-diphenylbenzene, and the solid phenanthrene were measured by the transpiration method using the nitrogen stream [16]. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted saturator. At constant temperature (±0.1 K), a stream of $N_2$ was passed through the saturator and the transported material was collected in a cold trap. The absolute vapor pressures $p_i$ at different temperatures $T_i$ were calculated from the amount of product collected within a definite period of time according to the ideal gas law. The volume of transporting gas $V_{N_2}$ was determined from the flow rate and time of measurements. Vaporization or sublimation enthalpies were derived from the temperature dependences of the experimental vapor pressures (see Table 2).

### 2.6. Quartz crystalline microbalance (QCM): sublimation enthalpy measurements

Sublimation enthalpies of the solid samples of 1,2,3,4-tetraphenylnaphthalene, hexaphenylbenzene, and rubrene were derived from the temperature dependences of the experimentally measured change in the vibrational frequency of the quartz crystal.

**Table 2**
Results from measurements of the vapour pressure $p$ of aromatic hydrocarbons using the transpiration method.

| $T^{a}$ (K) | $m^{b}$ (mg) | $V_{(N2)}{}^{c}$ (dm$^3$) | Gas-flow (dm$^3$/h) | $p^{d}$ (Pa) | $(p_{exp}-p_{calc})$ (Pa) | $\Delta_l^g H_m/\Delta_{cr}^g H_m$ (kg mol$^{-1}$) |
|---|---|---|---|---|---|---|
| 1-Phenylnaphthalene ($l$) $\Delta_l^g H_m$ (298.15 K) = (82.7 ± 0.5) kJ mol$^{-1}$   $\ln(p/\text{Pa}) = \frac{343.3}{R} - \frac{111085.6}{R\times(T,K)} - \frac{95.2}{R}\ln\left(\frac{T,K}{298.15}\right)$ | | | | | | |
| 318.5 | 2.24 | 103.6 | 5.01 | 0.26 | 0.02 | 80.77 |
| 323.5 | 5.46 | 172.9 | 5.01 | 0.38 | −0.01 | 80.29 |
| 328.3 | 3.9 | 75.12 | 5.01 | 0.62 | 0.02 | 79.84 |
| 328.4 | 5.04 | 100.6 | 5.01 | 0.6 | 0 | 79.83 |
| 333.4 | 4.37 | 58.18 | 5.01 | 0.92 | −0.02 | 79.35 |
| 338 | 6.24 | 55.34 | 5.01 | 1.36 | −0.02 | 78.91 |
| 343.6 | 4.92 | 28.39 | 2.35 | 2.09 | −0.09 | 78.38 |
| 343.6 | 4.92 | 28.39 | 2.35 | 2.1 | −0.08 | 78.38 |
| 351 | 5.41 | 17.53 | 5.01 | 3.76 | −0.12 | 77.68 |
| 353.1 | 5.92 | 15.63 | 5.01 | 4.62 | 0.08 | 77.48 |
| 358.3 | 8.02 | 14.96 | 4.8 | 6.44 | −0.22 | 76.98 |
| 358.5 | 5.29 | 9.18 | 5.01 | 6.87 | 0.12 | 76.96 |
| 363 | 6 | 7.51 | 5.01 | 9.53 | 0.24 | 76.53 |
| 368.3 | 4.92 | 4.34 | 5.01 | 13.52 | 0.15 | 76.03 |
| 371 | 6.27 | 4.6 | 5.01 | 16.65 | 0.63 | 75.77 |
| Phenanthrene (cr) $\Delta_{cr}^g H_m$ (298.15 K) = (91.4 ± 0.4) kJ mol$^{-1}$   $\ln(p/\text{Pa}) = \frac{307.4}{R} - \frac{101458.73}{R\times(T,K)} - \frac{33.8}{R}\ln\left(\frac{T,K}{298.15}\right)$ | | | | | | |
| 306.2 | 0.23 | 66.3 | 5.06 | 0.05 | 0 | 91.11 |
| 309.4 | 0.34 | 69.5 | 4.98 | 0.07 | 0 | 91 |
| 313.2 | 0.14 | 16.9 | 5.06 | 0.12 | 0.01 | 90.87 |
| 316.3 | 0.14 | 12.8 | 5.06 | 0.16 | 0 | 90.77 |
| 319.3 | 0.15 | 9.87 | 5.06 | 0.21 | −0.01 | 90.67 |
| 322.3 | 0.2 | 8.96 | 4.98 | 0.31 | 0.01 | 90.57 |
| 325.2 | 0.21 | 6.81 | 4.98 | 0.43 | 0.03 | 90.47 |
| 329.2 | 0.25 | 5.39 | 4.98 | 0.63 | 0.03 | 90.33 |
| 328.4 | 0.19 | 4.86 | 4.98 | 0.55 | −0.01 | 90.36 |
| 334.2 | 0.46 | 6.28 | 5.06 | 1.01 | 0.01 | 90.16 |
| 330.7 | 0.32 | 6.16 | 5.06 | 0.73 | 0.02 | 90.28 |
| 337.2 | 0.41 | 4.22 | 5.06 | 1.35 | 0.03 | 90.06 |
| 340.3 | 0.49 | 3.79 | 5.06 | 1.78 | 0.01 | 89.96 |
| 343.4 | 0.41 | 2.49 | 5.06 | 2.29 | −0.08 | 89.85 |
| 346.3 | 0.5 | 2.28 | 5.06 | 3.06 | −0.03 | 89.76 |
| 349.4 | 0.53 | 1.81 | 5.06 | 4.03 | −0.04 | 89.65 |
| 352.4 | 0.57 | 1.43 | 5.06 | 5.45 | 0.17 | 89.55 |
| 355.5 | 0.54 | 1.05 | 5.06 | 7.05 | 0.15 | 89.44 |
| 359.2 | 0.27 | 0.413 | 1.1 | 9.07 | −0.34 | 89.32 |
| 356.8 | 0.31 | 0.559 | 1.1 | 7.6 | −0.11 | 89.4 |
| 358.6 | 0.75 | 1.14 | 5.06 | 9.14 | 0.18 | 89.34 |
| 362.3 | 0.32 | 0.376 | 1.1 | 11.71 | −0.45 | 89.21 |
| 365.3 | 0.37 | 0.33 | 1.1 | 15.34 | −0.18 | 89.11 |
| 368.3 | 0.46 | 0.321 | 1.1 | 19.88 | 0.18 | 89.01 |
| 370.4 | 0.56 | 0.339 | 1.1 | 22.98 | −0.25 | 88.94 |
| 1,2-Diphenylbenzene ($l$) $\Delta_l^g H_m$ (298.15 K) = (86.0 ± 0.2) kJ mol$^{-1}$   $\ln(p/\text{Pa}) = \frac{361.5}{R} - \frac{117565.6}{R\cdot(T,K)} - \frac{105.8}{R}\ln\left(\frac{T,K}{298.15}\right)$ | | | | | | |
| 343.5 | 0.83 | 5.3 | 3.09 | 1.66 | 0.01 | 81.23 |
| 345.5 | 0.6 | 3.33 | 4 | 1.95 | 0 | 81.02 |
| 346.4 | 0.7 | 3.56 | 1.68 | 2.1 | 0 | 80.92 |
| 348.4 | 0.6 | 2.6 | 4 | 2.5 | 0.04 | 80.71 |
| 349.5 | 0.6 | 2.39 | 3.11 | 2.7 | 0.01 | 80.59 |
| 351.5 | 0.57 | 1.93 | 4 | 3.15 | 0 | 80.38 |
| 352.5 | 0.55 | 1.75 | 4.04 | 3.39 | −0.01 | 80.28 |
| 355.4 | 0.56 | 1.4 | 3.11 | 4.27 | 0.02 | 79.97 |
| 358.4 | 0.56 | 1.14 | 4.04 | 5.28 | −0.06 | 79.65 |
| 360.4 | 0.31 | 0.53 | 1.67 | 6.2 | 0.01 | 79.44 |
| 361.4 | 0.61 | 1 | 4 | 6.58 | −0.09 | 79.33 |
| 361.5 | 0.58 | 0.934 | 3.11 | 6.64 | −0.07 | 79.32 |
| 363.2 | 0.57 | 0.82 | 2.24 | 7.52 | −0.07 | 79.14 |
| 365.4 | 0.55 | 0.663 | 1.02 | 8.88 | −0.01 | 78.91 |
| 366.4 | 0.56 | 0.642 | 1.67 | 9.43 | −0.1 | 78.81 |
| 368.4 | 0.69 | 0.676 | 2.05 | 10.95 | −0.03 | 78.59 |
| 369.4 | 0.64 | 0.586 | 1.64 | 11.87 | 0.11 | 78.49 |
| 371.4 | 0.55 | 0.438 | 1.01 | 13.63 | 0.13 | 78.28 |
| 373.3 | 0.54 | 0.383 | 1 | 15.27 | −0.09 | 78.08 |
| 374.4 | 0.72 | 0.462 | 1.01 | 16.77 | 0.23 | 77.96 |
| 376.3 | 0.52 | 0.3 | 1 | 18.69 | −0.06 | 77.76 |
| 377.4 | 0.58 | 0.307 | 1.02 | 20.37 | 0.21 | 77.64 |

<sup>a</sup> is shown as footnote marker:

[a] Temperature of saturation.
[b] Mass of transferred sample $m$ condensed at $T = 273$ K.
[c] Volume of nitrogen $V_{(N2)}$ used to transfer mass $m$ of sample.
[d] Vapour pressure $p$ at temperature $T$ calculated from $m$ and the residual vapour pressure at $T = 273$ K. Vapour pressures derived from the transpiration method were reliable within (1–3)%.

The experimental setup was developed for measuring of compounds with the extremely low vapor pressures. Experimental procedure was tested with ionic liquids (ILs) and reported recently [17]. This technique is principally different from the well-established Knudsen-technique. In contrast to the Knudsen method, where the sample cell is closed with a membrane and only a small hole connects the sample container to the vacuum, in our method a sample of an aromatics is placed in an open cavity (Langmuir evaporation) inside of the thermostatted block and it is exposed to vacuum ($10^{-5}$ Pa) with the whole open surface of the loaded compound. The QCM is placed directly over the measuring cavity containing the sample. During the vaporization into vacuum, a certain amount of sample is deposited on the quartz crystal. The change in the vibrational frequency of the crystal, $\Delta f$, (which is a measure of an amount of sample deposited on the cold QCM) was recorded as function of time at different temperatures of the sample. Sublimation enthalpies were derived from the temperature dependences of the experimental $\Delta f$ values (see Table S4).

### 2.7. Thermogravimetric approach (TGA): sublimation enthalpy measurements

Sublimation enthalpy of the solid 1,2,3,4-tetraphenylnaphthalene was derived from the mass-loss temperature dependence measured by a commercial PerkinElmer Pyris 6 TGA. A plane platinum crucible with about 70 mg of the sample was used. Prior to the measurement of vaporization enthalpy, a careful conditioning of the sample inside the TGA was performed. For the removal of volatile impurities a heating ramp of 10 K min$^{-1}$ was used, followed by a 4 h static hold period at 423 K, continued with stepwise isothermal runs. Isothermal gravimetric analysis curves were measured in the temperature range 440–470 K at a N$_2$ flow rate of 140 mL min$^{-1}$. In order to trace any possible effect of impurities on the measured mass loss rate $dm/dt$ a typical experiment was performed in a few consecutive series with increasing and decreasing temperature steps. The detailed procedure has been described elsewhere [18]. The experimental mass loss rates $dm/dt$ temperature dependence for 1,2,3,4-tetraphenylnaphthalene are listed in Table S5.

### 3. Methodology

According to the IUPAC definition [19], dissolution is an interaction of a solute with the solvent, which leads to surrounding of the solute species in the solution. The molar enthalpy of solution $\Delta_{soln}H^{A_i/S}$ is the enthalpy change when 1 mole of a solute $A_i$ dissolves in sufficient amount of solvent $S$ to give a solution of infinite dilution. The molar enthalpy of solvation $\Delta_{solv}H^{A_i/S}$ is the enthalpy change when 1 mole of gaseous molecules of a solute $A$ dissolves in a solvent $S$ to give a solution of infinite dilution. Enthalpy of solvation $\Delta_{solv}H^{A_i/S}$ and enthalpy of solution $\Delta_{soln}H^{A_i/S}$ of any solute $A_i$ in a solvent $S$ are related over the molar enthalpy of vaporization $\Delta_l^g H_m^{A_i}$ for liquid solutes and over the molar sublimation enthalpy ($\Delta_{cr}^g H_m^{A_i}$) for solid solutes as follows:

$$\Delta_{solv}H^{A_i/S} = \Delta_{soln}H^{A_i/S} - \Delta_l^g H_m^{A_i}, \tag{3}$$

$$\Delta_{solv}H^{A_i/S} = \Delta_{soln}H^{A_i/S} - \Delta_{cr}^g H_m^{A_i}. \tag{4}$$

Thus, use of Eqs. (3) and (4) opens an independent way to assess vaporization/sublimation enthalpy of any solute $A_i$ provided that the solvation and solution enthalpies are available. Indeed, the solution enthalpy $\Delta_{soln}H^{A_i/S}$ in different solvents can be measured by using the solution calorimetry at 298.15 K. Furthermore, our systematic experimental and theoretical work on $\Delta_{solv}H^{A_i/S}$

[9,10,20–22], spanning more than three decades, has allowed detecting some general trends that are now useful for the evaluation of vaporization/sublimation enthalpies. It has turned out that a remarkable linear dependence exists between enthalpies of solvation of solutes $A_i$ in non-polar or polar solvents and their molar refractions (MR$^{A_i}$). The most extended study was performed with cyclohexane as the solvent [9,10,20]. Different organic non-electrolyte compounds from water to diphenylmercury (altogether 102 molecules) fit a linear equation (Eq. (5)) [20]:

$$-\Delta_{solv}H^{A_i/c-C_6H_{12}} = 5.09 + 1.03 \\ \times MR^{A_i}(N = 102; R = 0.994; SD = 1.56 \text{ kJ mol}^{-1}). \tag{5}$$

The general linear correlation between enthalpy of solvation in cyclohexane and molar refraction of solutes has a theoretical basis. Solvation is the process of transfer of solute molecules from the gaseous state, where intermolecular interactions are practically absent compared to liquids. Hence, $\Delta_{solv}H^{A_i/S}$ values characterize the overall energy of solute-solvent interactions. In the case of cyclohexane solutions, solute-solvent interactions include only dispersion forces. The energy of dispersion interactions linearly depends on polarizabilities of interacting molecules. Following, when we dissolve different compounds in one solvent, enthalpy of solvation should be linearly dependent on polarizabilities of solutes. At the same time polarizability values and MR values are related through Eq. (6):

$$MR^{A_i} = \frac{4}{3} \times \pi \times N \times \alpha, \tag{6}$$

where $N$ is the Avogadro's constant and $\alpha$ is the molar polarizability. Thus, the enthalpy of solvation in cyclohexane should be linearly dependent on the molar refraction. The dipole moment of solute molecules does not affect the linearity of $\Delta_{solv}H^{A_i/S}$ vs. MR$^{A_i}$ relationship in absence of any specific interactions like hydrogen bonds or other donor-acceptor interactions with solvent. It was shown that solvation enthalpies of isomeric molecules which have differences in dipole moments up to 5.8D (cis- and trans-dichloroethylenes, cis- and trans-dicyano-ethylenes; o-, m-, and p-dichlorobenzenes; o-, m-, and p-dinitrobenzenes and etc.) are practically equal [20].

The linear relationship between the enthalpy of solvation and MR$^{A_i}$ is universally observed for hydrocarbons as solvents [21]. Since the solubilities of polyaromatic hydrocarbons (PAHs) in cyclohexane are generally very poor, a more suitable linear correlation has been developed for benzene as the solvent (Eq. (7)) [22]:

$$-\Delta_{solv}H^{A_i/C_6H_6} = 6.86 + 1.088 \\ \times MR^{A_i} (N \\ = 11; R = 0.998; SD = 0.8 \text{ kJ mol}^{-1}). \tag{7}$$

Experimental data (see Table S3) for benzene, fluorobenzene, chlorobenzene, bromobenzene, 1,2- and 1,4-dichlorobenzenes, iodobenzene, naphthalene, 1-chloronaphthalene, biphenyl, and anthracene were used to establish coefficients of Eq. (7). Now, using enthalpies of solvation calculated with Eq. (7) and enthalpies of solution of PAHs measured in benzene, their enthalpies of vaporization/sublimation at 298.15 K can be derived as follows:

$$\Delta_l^g H^{A_i} = \Delta_{soln}H^{A_i/C_6H_6} + 6.86 + 1.088 \times MR^{A_i}, \tag{8}$$

$$\Delta_{cr}^g H^{A_i} = \Delta_{soln}H^{A_i/C_6H_6} + 6.86 + 1.088 \times MR^{A_i}. \tag{9}$$

With full respect to well established conventional techniques, the calculation of vaporization/sublimation enthalpies according to Eqs. (8) and (9) suggests an additional valuable option for data evaluation especially for thermally unstable compounds, because

the solution measurements are carried out directly at 298.15 K. As a consequence, the ambiguous heat capacity adjustments of vaporization/sublimation enthalpies to the reference temperature are not required. It is also important, that only about 0.5–1.0 g of sample are enough for a set of measurements. Moreover, the solution experiment can be completed within a few hours as it is independent of the size and the volatility of the solute, which impacts significantly in the duration of conventional experiments. Depending on a favorable solubility of a molecule of interest in cyclohexane or in benzene, the linear correlations (Eqs. (5) and (7)) can be used for the evaluation of vaporization/sublimation data. An example of step-by-step sublimation enthalpy calculations according to the solution calorimetry approach presented in this work is given in the Supporting Material. The calculated errors of enthalpies of sublimation and vaporization with Eqs. (8) and (9) has been assessed to be less than 2–3 kJ mol$^{-1}$. This estimate is the sum of uncertainties of the enthalpy of solution and the molar refraction determinations.

## 4. Results and discussion

For this study, we selected 18 aromatic compounds (Table 1). Our choice has been primarily motivated by collecting molecules of possibly broad variations in structure: from sterically hindered phenyl substituted benzenes and naphthalenes to polycyclic aromatics. Enthalpies of vaporization/sublimation of PAHs were determined by Eqs. (7)–(9) based on their experimentally measured enthalpies of solution in benzene and molar refractions (see Table 1). Molar refractions of diphenylacetylene, 1,3-diphenylbenzene, 1,2,3-triphenylbenzene, 9-phenylanthracene, 9,10-diphenylanthracene and 1,2,3,4-tetraphenylnaphthalene were measured in this work, values of other studied molecules were evaluated from the literature data [23–28] (for more details see Supporting Material).

For validation of the solution calorimetry approach, we collected experimental $\Delta_{cr}^{g} H_m / \Delta_l^{g} H_m$ data available in the literature. Six compounds have been additionally studied in Rostock using "conventional" methods (Table 3).

Transpiration is the well established method for measurement of absolute vapor pressures especially of thermally labile compounds because the sample in the saturator stands always under protection of N$_2$ stream. However, for low volatile compounds like PAHs, this method becomes very time consuming. In order to expedite experiments, it is desirable to increase the gas flow over sample, as long as the flow rate is not too fast in order to reach the saturation of the nitrogen stream with a compound. We tested our setup with measurements on phenanthrene. The upper limit for our apparatus where the gas flow rate could already disturb the equilibration was at a flow rate of 7.0 dm$^3$ h$^{-1}$. Thus, we carried out the experiments at flow rates below this limit to be sure that transporting gas was in saturated equilibrium with the coexisting liquid or solid phase in the saturation tube. The enthalpy of sublimation of phenanthrene, $\Delta_{cr}^{g} H_m$ (298.15 K) = 91.4 ± 0.4 kJ mol$^{-1}$ (see Table 2), measured by transpiration in this work is in good agreement with the recommended value $\Delta_{cr}^{g} H_m$ (298.15 K) = (92.1 ± 0.6) kJ mol$^{-1}$ [5].

For 1-phenylnaphthalene we measured by transpiration $\Delta_l^{g} H_m^{A_i}$ (298.15 K) = (82.7 ± 0.5) kJ mol$^{-1}$ in order to ascertain the single value $\Delta_l^{g} H_m^{A_i}$ (298.15 K) = (81.0 ± 1.8) kJ mol$^{-1}$ available from the drop microcalorimetric method [29]. After completing of experiments on 1-phenylnaphthalene we become aware of indistinguishable ebulliometric result (see Table 3) reported just recently [30]. The sublimation enthalpies of 1,2-diphenylbenzene available in the literature spreads from 101 to 105 kJ mol$^{-1}$. In order to check this value, we measured the vaporization enthalpy $\Delta_l^{g} H_m^{A_i}$ (298.15 K) = (86.0 ± 0.2) kJ mol$^{-1}$ (see Table 2) by transpiration. Using the enthalpy of fusion at 298.15 K $\Delta_l^{cr} H_m^{A_i}$ = (15.2 ± 0.7) kJ

mol$^{-1}$ reported for 1,2-diphenylbenzene [5] we calculated the enthalpy of sublimation for this compound $\Delta_{cr}^{g} H_m^{A_i} = \Delta_l^{g} H_m^{A_i} + \Delta_l^{cr} H_m^{A_i}$ = (86.0 + 15.2) = 101.2 ± 0.9 kJ mol$^{-1}$ (see Table 3).

The single value $\Delta_{cr}^{g} H_m^{A_i}$ (298.15 K) = (161.4 ± 1.4) kJ mol$^{-1}$ for 1,2,3,4-tetraphenylnaphthalene reported from the ME–QCM study [31] was proved in this work with QCM and TGA measurements. The results are indistinguishable (see Table 3) within the experimental uncertainties.

The enthalpy of sublimation of hexaphenylbenzene $\Delta_{cr}^{g} H_m^{A_i}$(298.15 K) = (196.6 ± 1.0) kJ mol$^{-1}$ measured in this work by QCM was in agreement with the result (195.4 ± 6.7 kJ mol$^{-1}$) derived from thermogravimetry [33] and the value (195.9 ± 2.2 kJ mol$^{-1}$) measured by solution calorimetry in this work. However, the recent result measured by combination of the Knudsen method with the QCM [32] was lower by 10 kJ mol$^{-1}$. Our study was performed at lower temperatures and in the broader temperature range in comparison with the ME–QCM study [32]. Such a discrepancy could be ascribed to a possible second order solid phase transitions within the temperature range of the QCM (this work) or ME–QCM [32] study. In order to detect this phase transition we studied our sample from room temperature to the melting point by the DSC. We have observed the solid phase transitions with the ongoing temperature 533.3 K prior to melting (see Fig. S1 in Supporting Material). However this transition was outside of temperature ranges used in Refs. [32,33] as well as in this work.

The value $\Delta_{cr}^{g} H_m^{A_i}$ (298.15 K) = 178.2 kJ mol$^{-1}$ available for rubrene [7] was significantly different from our QCM result $\Delta_{cr}^{g} H_m^{A_i}$ (298.15 K) = (213.9 ± 1.3) kJ mol$^{-1}$. However the solution calorimetry result $\Delta_{cr}^{g} H_m^{A_i}$ (298.15 K) = (213.2 ± 2.0) kJ mol$^{-1}$ favours the QCM result from this work.

Experimental data on vaporization/sublimation enthalpies at 298.15 K available from the literature are usually adjusted in the different way. In this work we collected the original vapor pressures and treated them uniformly. All available temperature dependent $p_i$ data were fitted using following equation [16]:

$$R \times \ln p_i = a + \frac{b}{T} + \Delta_{cr}^{g} C_p \times \ln \left( \frac{T}{T_0} \right), \qquad (10)$$

where $a$ and $b$ are adjustable parameters and $\Delta_{cr}^{g} C_p$ is the difference of the molar heat capacities of the gaseous and the solid phases, respectively. $T_0$ appearing in Eq. (10) is an arbitrarily chosen reference temperature (set to 298.15 K here). Consequently, from Eq. (10) the expression for the sublimation enthalpy (or $\Delta_{cr}^{g} H_m^{A_i}$) at temperature $T$ = 298.15 K is derived:

$$\Delta_{cr}^{g} H_m^{A_i}(T) = -b + \Delta_{cr}^{g} C_p \times T. \qquad (11)$$

Eqs. (10) and (11) are also valid for the study of the liquid samples. For this case the enthalpy of vaporization is derived from Eq. (11) by using the appropriate values of $\Delta_l^{g} C_p$. Values of $\Delta_{cr}^{g} C_p$ and $\Delta_l^{g} C_p$ have been calculated according to the procedure developed by Chickos et al. [3]. We used available experimental isobaric molar heat capacities $C_p^{cr}$ and $C_p^l$ of aromatic compounds to calculate $\Delta_{cr}^{g} C_p$ and $\Delta_l^{g} C_p$ or estimated them by the group-contribution method [34].

The available vaporization/sublimation enthalpies at 298.15 K for the 18 aromatic compounds are compiled in Table 3. We carefully analyzed the primary references with respect to purity of samples and experimental conditions. This analysis enables assessment of the reliability of available data in order to calculate the averaged values used in this work for validation of the solution calorimetry procedure. The selected values are given in Table 3 in bold. These values were taken for comparison with the vaporization/sublimation enthalpies derived from the solution calorimetry (Table 1). As can be seen from the last column of Table 1 the results

**Table 3**

Compilation of data on enthalpies of sublimation, $\Delta^g_{cr}H^{A_i}_m$, and enthalpies of vaporization, $\Delta^g_l H^{A_i}_m$, of aromatic hydrocarbons.

| Compounds | Technique[a] | T-range (K) | $\Delta^g_{cr}H^{A_i}_m/\Delta^g_l H^{A_i}_m$ $T_{av}$ (kJ mol⁻¹) | $C^{cr}_p$ $(-\Delta^g_{cr}C_p)$ $C^l_p$ $(-\Delta^g_l C_p)$[b] (J mol⁻¹ K⁻¹) | $\Delta^g_{cr}H^{A_i}_m/\Delta^g_l H^{A_i}_m$[c] 298.15 K (kJ mol⁻¹) | Refs. |
|---|---|---|---|---|---|---|
| Azulene (cr) | ME | 253–293 | 75.8 | 157.0 (24.3) | *75.2 ± 2.0* | [7] |
| | ME + S | 293–323 | – | | 95.4 ± 0.4 | [35] |
| | | 290–372 | 82.8 | | 83.5 | [36] |
| | HSA | 283.3–325.6 | 78.4 | | 78.6 | [37] |
| | CGC | | | | *72.7 ± 2.0* | [37] |
| | S | 321.0–371.0 | 70.9 | | 72.0 ± 1.4 | [38] |
| | C | 298.15 | | | 76.8 ± 0.2 | [39] |
| | | | | | **74.2 ± 2.2** | Average |
| | SC | 298.15 | | | 73.3 ± 0.7 | This work |
| Diphenylacetylene (cr) | ME | 317 | 88.7 | 240.3(53.2) | *89.7 ± 4.6* | [40] |
| | HSA | 299–321 | 90.4 | | *91.0 ± 4.6* | [41] |
| | ME | | | | *95.1 ± 1.1* | [42] |
| | | | | | **91.9 ± 3.2** | Average |
| | SC | 298.15 | | | 92.5 ± 1.0 | This work |
| Phenanthrene (cr) | T | 306.2–370.4 | 90.1 | 220.3(33.8) | 91.4 ± 0.4 | This work |
| | | | | | 92.1 ± 0.6 | [5] |
| | | | | | **92.1 ± 0.6** | Selected |
| | SC | 298.15 | | | 92.3 ± 0.7 | This work |
| *trans*-Stilbene (cr) | ME | 329 | 90.8 | 235.0(36.0) | 91.9 ± 0.8 | [40] |
| | TCM | 303–315 | 86.5 | | 86.9 ± 0.3 | [43] |
| | C | 298.15 | | | 99.2 ± 0.4 | [39] |
| | TCM | 295–318 | 102.1 | | 102.4 ± 0.6 | [44] |
| | TE, S | 297.5–364.5 | 100.6 | | 101.6 ± 0.2 | [45] |
| | T | 293–338 | 103.8 | | 104.4 ± 2.5 | [46] |
| | N/A | 298–343 | | | 100.3 | [36] |
| | K | 298–357 | 101.1 | | 102.1 ± 0.3 | [47] |
| | T | 324.3–367.0 | 100.2 | | 102.0 ± 0.4 | [48] |
| | | | | | **101.7 ± 1.2** | Average |
| | SC | 298.15 | | | 102.8 ± 0.9 | This work |
| 1-Phenylnaphthalene (*l*)[d] | DC | 386 | 104.0 | 325.6(95.2) | *81.0 ± 1.8* | [29] |
| | T | (323–383) | 88.6 | | *93.8* | [49] |
| | IP, E | 375–630 | | | *82.1 ± 0.5* | [30] |
| | T | 318.5–371.0 | 78.4 | | *82.7 ± 0.5* | This work |
| | | | | | **81.9 ± 1.0** | Average |
| | SC | 298.15 | | | 82.7 ± 0.8 | This work |
| Pyrene (cr) | ME | 342.1–358.4 | 94.6 | 229.4(25.4) | *95.9 ± 1.2* | [50] |
| | ME | 298–363 | 100.5 | | *101.3* | [7] |
| | ME | | | | *95.7* | [51] |
| | C | 348–419 | 97.5 | | *99.7 ± 2.0* | [51] |
| | IP | 348–419 | 97.7 | | *99.9 ± 0.5* | [52] |
| | – | 398.2–423.2 | 94 | | *96.8 ± 0.2* | [36] |
| | – | 298–401 | | | *98.3* | [36] |
| | S | 360–419 | | | *103.5* | [53] |
| | K | 353.3–423 | 97.6 | | *99.9 ± 0.6* | [54] |
| | T | (353–403) | 97.9 | | *99.9* | [49] |
| | ME | 320.1–366.2 | 103.1 | | *104.2 ± 3.9* | [55] |
| | ME | 352 | 97.5 | | *98.9 ± 1.7* | [56] |
| | T | 283–323 | 91.2 | | *91.3 ± 0.5* | [57] |
| | ME | 322.0–381.4 | 97.8 | | *99.1 ± 1.3* | [58] |
| | S | | | | *99.3* | [59] |
| | ME | 341.4–408.1 | 103.5 | | *105.4 ± 2.8* | [60] |
| | | | | | **99.3 ± 1.8** | Average |
| | SC | 298.15 | | | 103.8 ± 0.9 | This work |
| Fluoranthene (cr) | ME | 298–358 | 102.5 | 230 (26.9) | *103.3* | [7] |
| | ME | 329.0–353.6 | 102.2 | | *103.3 ± 3.4* | [61] |
| | T | 283–323 | 84.6 | | *84.7 ± 0.9* | [57] |
| | T | (353–403) | 98.3 | | *100.5* | [49] |
| | – | | | | *99.0* | [36] |
| | CGC | | | | *99.4* | [62] |
| | CGC | | | | *93.3* | [63] |
| | CGC | | | | *100.8 ± 2.6* | [64] |
| | ME | 326.8–359.2 | 97.0 | | *98.1 ± 1.3* | [58] |
| | C | 298.15 | | | *99.2 ± 0.8* | [39] |
| | | | | | **100.5 ± 1.4** | Average |
| | SC | 298.15 | | | 102.8 ± 0.9 | This work |
| 1,2-Diphenylbenzene (cr) | S | | | 274.7(42.0) | *103.1 ± 0.1*[e] | [65] |
| | | | | | *105.2 ± 5.0*[e] | [36] |
| | ME | 312.3–328.6 | 102.8 | | *103.7 ± 0.6* | [66] |
| | T | | | | *101.6 ± 0.3*[e] | [67] |
| | T | | | | *101.2 ± 0.7*[e] | This work |
| | | | | | **103.0 ± 1.4** | Average |
| | SC | 298.15 | | | 105.7 ± 1.0 | This work |
| 1,3-Diphenylbenzene (cr) | | 313–363 | 118.9 | 277.4(42.4) | 120.6 | [7] |
| | T | 328.6–358.2 | 115.6 | | *117.5 ± 1.2* | [67] |

**Table 3** (Continued)

| Compounds | Technique[a] | T-range (K) | $\Delta_{cr}^g H_m^{A_l}/\Delta_l^g H_m^{A_l}$ $T_{av}$ (kJ mol⁻¹) | $C_p^{cr}$ $(-\Delta_{cr}^g C_p)$ $C_p^l$ $(-\Delta_l^g C_p)$[b] (J mol⁻¹ K⁻¹) | $\Delta_{cr}^g H_m^{A_l}/\Delta_l^g H_m^{A_l}$[c] 298.15 K (kJ mol⁻¹) | Refs. |
|---|---|---|---|---|---|---|
| | ME | 337.3–359.1 | 116.7 | | *118.8 ± 0.5* | [66] |
| | | | | | **118.2 ± 1.4** | Average |
| | SC | 298.15 | | | 115.5 ± 0.2 | This work |
| 1,4-Diphenylbenzene (cr) | ME | 333–393 | 120.6 | 279.6(42.7) | *123.4 ± 2.0* | [7] |
| | ME | 338–431 | 118.9 | | *122.6 ± 2.0* | [68] |
| | ME | 373.3–395.3 | 122.5 | | *126.1 ± 0.4* | [66] |
| | CGC | | | | *123.0 ± 8.8*[e] | [69] |
| | T | 328.6–358.2 | 115.6 | | *124.1 ± 1.6* | [67] |
| | | | | | **123.8 ± 1.2** | Average |
| | SC | 298.15 | | | 121.3 ± 1.2 | This work |
| 1,2-Benzanthracene (cr) | ME | 333–393 | 119.6 | 273.6(39.3) | 122.2 | [7] |
| | ME | 377–400 | 104.6 | | 108.1 | [70] |
| | ME | 365–450 | 121.2 | | 125.5 | [68] |
| | TE | 377–426 | 103.9 | | 108.0 ± 3.8 | [71] |
| | T | 353–403 | 115.5 | | 118.6 | [49] |
| | ME | 330–390 | 113.5 | | *115.9 ± 2.3* | [72] |
| | ME + TE | 373–396 | 113.1 | | *116.5 ± 1.0* | [73] |
| | | | | | **116.2 ± 0.6** | Average |
| | SC | 298.15 | | | 116.2 ± 0.9 | This work |
| 9-Phenylanthracene (cr) | | 353–426 | 115.3 | 296.0(45.2) | *119.4 ± 5.0* | [74] |
| | TE/HSA | 353–383 | 116.9 | | *120.1 ± 1.2* | [75] |
| | | 353–426 | 115.2 | | *119.2 ± 5.0* | [36] |
| | | | | | *120.2 ± 1.2*[e] | [75] |
| | | | | | *120.4 ± 5.0*[e] | [36] |
| | T | 353–403 | 118.7 | | *122.3 ± 3.0* | [49] |
| | | | | | **120.3 ± 0.8** | Average |
| | SC | 298.15 | | | 125.5 ± 0.4 | This work |
| 1,2,3-Triphenylbenzene (cr) | ME–QCM | 373.2–395.0 | 132.1 | 358.0 (54.5) | 136.8 ± 0.8 | [76] |
| | SC | 298.15 | | | 138.6± 0.7 | This work |
| 1,2,5,6-Dibenzanthracene (cr) | T | 353–423 | 134.1 | 313.0(47.7) | 138.4 | [49] |
| | TE, ME | 436–462 | 141.6 | | *148.0 ± 4.0* | [73] |
| | ME | 403–512 | 142.0 | | *149.0 ± 2.3* | [68] |
| | | | | | **148.5 ± 1.0** | Average |
| | SC | 298.15 | | | 148.3 ± 1.5 | This work |
| 9,10-Diphenylanthracene (cr) | ME | 393–433 | 143.6 | 383.0 (58.2) | *150.3 ± 3.0* | [7] |
| | HSA | 481–502 | 156.9 | | *168.2 ± 4.2* | [77] |
| | T | (353–403) | 137.5 | | *142.2 ± 3.0* | [49] |
| | QCM | 341 – 373 | 149.3 | | **153.6 ± 0.8** | Average |
| | SC | 298.15 | | | 152.9 ± 1.0 | This work |
| 1,2,3,4-Tertra-phenylnaphthalene (cr) | ME–QCM | 430.3–448.3 | 150.9 | 491.6(74.5) | *161.4 ± 1.4* | [31] |
| | QCM | 338.1–370.6 | 156.2 | | *160.4 ± 0.8* | This work |
| | TGA | 440–470 | 147.3 | | *158.9 ± 1.4* | This work |
| | | | | | **160.2 ± 1.6** | Average |
| | SC | 298.15 | | | 164.8 ± 1.7 | This work |
| Hexaphenylbenzene (cr) | ME–QCM | 491.4–510.5 | 166.9 | 627 (94.8) | 186.1 ± 3.2 | [32] |
| | TGA | 573–603 | 167.9 | | 195.4 ± 6.7 | [33] |
| | QCM | 445.6–493.6 | 180.4 | | 196.6 ± 1.0 | This work |
| | | | | | **196.6 ± 1.0** | Selected |
| | SC | 298.15 | | | 195.9 ± 2.2 | This work |
| 5,6,11,12-Tetraphenylnaphthacene (rubrene) (cr) | ME | 453–523 | 160.7 | 609.0 (92.1) | 178.2 | [7] |
| | QCM | 450.5–490.7 | 198.0 | | 213.9 ± 1.3 | This work |
| | | | | | **213.9 ± 1.3** | Selected |
| | SC | 298.15 | | | 213.2 ± 2.0 | This work |

[a] Techniques – C: calorimetry; CGC: correlation-gas chromatography; DC: drop calorimetry; E: ebulliometry; HSA: head space analysis; IP: inclined piston manometry; ME: mass effusion-Knudsen; ME–QCM: combined mass effusion-Knudsen effusion and quartz crystal microbalance; QCM: quartz crystal microbalance; S: static method; SC: solution calorimetry; T: transpiration method; TCM: thermal conductivity manometers; TE: torsion effusion; TGA: thermogravimetric approach.

[b] The molar heat capacities, $C_p^{cr}$ and $C_p^l$, and the difference between solid or liquid and gaseous phases ($\Delta_{cr}^g C_p$, $\Delta_l^g C_p$) required for adjustment to 298.15 K. The $\Delta_{cr}^g C_p$ and $\Delta_l^g C_p$ values were estimated by Chickos et al. [3] method from the experimental heat capacities $C_p^{cr}$, taken from http://webbook.nist.gov/chemistry/ or calculated by Chickos and Acree group-contribution method [34].

[c] Uncertainties were expressed as standard deviation. Values taken into account are given in italic.

[d] For the liquid state we used $C_p^l$ ($\Delta_l^g C_p$) and vaporization enthalpy $\Delta_l^g H_m$.

[e] Calculated as the sum $\Delta_{cr}^g H_m = \Delta_l^g H_m + \Delta_{cr}^l H_m$ with values of fusion enthalpies taken from [5].

derived from solution calorimetry are in good agreement with those measured by conventional methods. The average deviation of 1.8 kJ mol⁻¹ for 18 entries in Table 1 is quite comparable with the uncertainties ascribed to the experimental values. Only for three molecules from the list (pyrene, 9-phenylanthracene, and 1,2,3,4-tetraphenylnaphthalene), the results from solution calorimetry are ∼4–5 kJ mol⁻¹ higher. The reason for these deviations is not quite

apparent and it could be ascribed to accumulation of uncertainties of the methods applied. For example, for 9-phenylanthracene most of experimental values have uncertainties of 3–5 kJ mol⁻¹ and could be the explanation for this outlier. At the same time, for the largest molecules from the set, hexaphenylbenzene and rubrene, the agreement of results between conventional methods and solution calorimetry is exact. Comparison of vaporization/
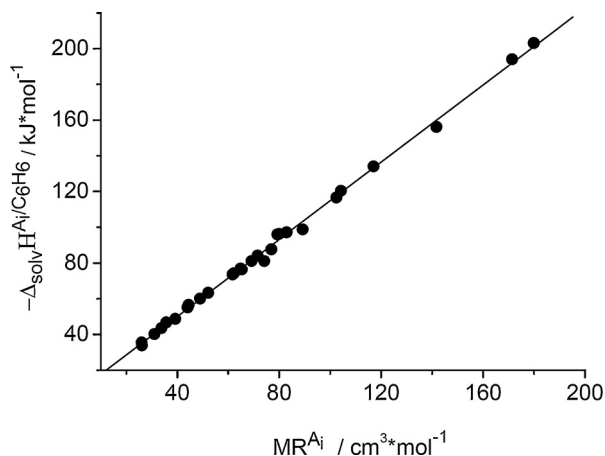
**Fig. 1.** Correlation between solvation enthalpies in benzene of aromatic hydrocarbons and their molar refraction values.

sublimation enthalpies derived from the solution calorimetry approach with those measured by conventional methods has shown good performance of this complementary method by using of empirical Eq. (7). It should be noted that coefficients of the Eq. (7) were calculated in Ref. [22] from experimental data for 11 aromatic hydrocarbons and their halogen derivatives. The largest in this series of solutes was anthracene. However, for further applications it is important to prove how universal Eq. (7) be towards hydrocarbons with different structures. We used new results discussed in this work for this purpose. Vaporization/sublimation enthalpies selected in Table 3 and new experimental enthalpies of solution (Table 1) were used to derive enthalpies of solvation, $\Delta_{solv}H^{A_i/S}$, of 18 aromatic hydrocarbons in benzene (see Table S6 in Supporting Material). We plotted $\Delta_{solv}H^{A_i/S}$ vs. $MR^{A_i}$ values for the extended set of 29 aromatic compounds (see Fig 1, data are from Table S6 in Supporting Material). As expected, an excellent linear correlation ($N = 29$; $R = 0.99$; $SD = 2.1$) was observed with coefficients identical to those given in Eq. (7). It is also worth mentioning that in contrast to the restricted data set used in Ref. [22] the range of molar refractions used in the current study for the linear data approximation was almost three times larger. This fact was an evidence that correlation between the solvation enthalpy in benzene and the molar refraction remains valid for this extended set of aromatic hydrocarbons and their halogen derivatives regardless of their size and structure.

### 4.1. Summary of benefits for using solution calorimetry for evaluation of $\Delta_{cr}^{g}H_m/\Delta_l^{g}H_m$

There are several very important advantages of using the solution calorimetry for the indirect evaluation of the vaporization/sublimation enthalpies of organic compounds:

- measurements using solution calorimetry are quick and less demanding as compared to conventional methods;
- purity and quantity requirements for the chemicals are less rigorous;
- results from solution calorimetry are derived directly at the reference temperature 298.15 K and the ambiguous temperature adjustments specific for conventional methods are not required;
- solution calorimetry is the method of choice for studies of thermally unstable and/or explosive compounds;
- the solution calorimeter is commercially available or can be easily constructed.

## 5. Conclusion

We have developed and tested a solution calorimetry approach for quick appraisal of vaporization/sublimation enthalpies of organic compounds. It was based on the linear dependence of solvation enthalpies of solutes in benzene and their molar refractions. This approach suggests the validity of the complementary thermochemical option for vaporization/sublimation data evaluation, which also permits the rapid gathering of reliable information for very low volatile chemicals. Enthalpies of vaporization and sublimation for 18 aromatic and polyaromatic hydrocarbons at 298.15 K derived by using solution calorimetry were in good agreement with the reliable results measured by conventional techniques. Unlike conventional methods, the solution calorimetry approach provides results directly at the reference temperature without heat capacity adjustments.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tca.2014.05.033.

## References

[1] V.N. Emel, 'yanenko, S.P. Verevkin, A. Heintz, The gaseous enthalpy of formation of the ionic liquid 1-butyl-3-methylimidazolium dicyanamide from combustion calorimetry, vapor pressure measurements, and ab initio calculations, J. Am. Chem. Soc. 129 (2007) 3930–3937.

[2] S.P. Verevkin, Phase changes in pure component systems: Liquids and gases, in: R.D. Weir, W. Th. De Loos (Eds.), Measurement of the Thermodynamic Properties of Multiple Phases, Elsevier, Amsterdam, 2005, pp. 6–30.

[3] J.S. Chickos, S. Hosseini, D.G. Hesse, J.F. Liebman, Heat capacity corrections to a standard state: a comparison of new and some literature methods for organic liquids and solids, Struct. Chem. 4 (1993) 271–277.

[4] S.P. Verevkin, D.H. Zaitsau, V.N. Emel'yanenko, A.V. Yermalayeu, Making sense of enthalpy of vaporization trends for ionic liquids: new experimental and simulation data show a simple linear relationship and help reconcile previous data, J. Phys. Chem. B 117 (2013) 6473–6486.

[5] M.V. Roux, M. Temprado, J.S. Chickos, Y. Nagano, Critically evaluated thermochemical properties of polycyclic aromatic hydrocarbons, J. Phys. Chem. Ref. Data 37 (2008) 1885–1996.

[6] M.J.S. Monte, L.M.N.B.F. Santos, M. Fulem, J.M.S. Fonseca, C.A.D. Sousa, New static apparatus and vapor pressure of reference materials: naphthalene, benzoic acid, benzophenone, and ferrocene, J. Chem. Eng. Data 51 (2006) 757–766.

[7] H. Hoyer, W. Peperle, Dampfdrunkmessungen an organischen substanzen und ihre sublimationswarmen, Z. Electrochem. 62 (1958) 61–66.

[8] A. Magnus, H. Hartmann, F. Becker, Verbrennungswarmen und resonanzenergien von mehrkernigen aromatischen kohlenwasserstoffen, Z. Phys. Chem. 197 (1951) 75–91.

[9] B.N. Solomonov, I.S. Antipin, V.V. Gorbatchuk, A.I. Konovalov, Solvation of organic compounds in non-polar media, Dokl. Akad. Nauk SSSR 247 (1979) 405–408.

[10] B.N. Solomonov, I.S. Antipin, V.B. Novikov, A.I. Konovalov, Solvation of organic compounds in cyclohexane. New method of estimating heats of evaporation of substances, Zh. Obshch. Khim. 52 (1982) 2681–2688.

[11] K.V. Zaitseva, M.A. Varfolomeev, V.B. Novikov, B.N. Solomonov, Enthalpy of cooperative hydrogen bonding in complexes of tertiary amines with aliphatic alcohols: calorimetric study, J. Chem. Thermodyn. 43 (2011) 1083–1090.

[12] K.V. Zaitseva, M.A. Varfolomeev, B.N. Solomonov, Thermodynamic functions of hydrogen bonding of amines in methanol derived from solution calorimetry data and headspace analysis, Thermochim. Acta 535 (2012) 8–16.

[13] D. Hallén, S.-O. Nilsson, W. Rothschild, I. Wadsö, Enthalpies and heat capacities for n-alkan-1-ols in H$_2$O and D$_2$O, J. Chem. Thermodyn. 18 (1986) 429–442.

[14] R. Sabbah, X.W. An, J.S. Chickos, M.L.P. Leitao, M.V. Roux, L.A. Torres, Reference materials for calorimetry and differential thermal analysis, Thermochim. Acta 331 (1999) 93–204.

[15] T. Sugiura, H. Ogawa, Thermodynamic properties of solvation of aromatic compounds in cyclohexane, heptane, benzene, 1,4-dioxane, and chloroform at 298.15 K, J. Chem. Thermodyn. 41 (2009) 1297–1302.

[16] D. Kulikov, S.P. Verevkin, A. Heintz, Enthalpies of vaporization of a series of aliphatic alcohols: experimental results and values predicted by the ERAS-model, Fluid Phase Equilib. 192 (2001) 187–207.

[17] S.P. Verevkin, D.H. Zaitsau, V.N. Emelyanenko, A. Heintz, A new method for the determination of vaporization enthalpies of ionic liquids at low temperatures, J. Phys. Chem. B 115 (2011) 12889–12895.

[18] S.P. Verevkin, R.V. Ralys, Dz.H. Zaitsau, V.N. Emel, 'yanenko, C. Schick, Express thermogravimetric method for the vaporization enthalpies appraisal for very low volatile molecular and ionic compounds, Thermochim. Acta 238 (2012) 55–62.

[19] IUPAC, Compendium of Chemical Terminology, in: A.D. McNaught, A. Wilkinson (Eds.), The Gold Book, 2nd ed., Blackwell Scientific Publications, Oxford, UK, 1997.

[20] B.N. Solomonov, V.B. Novikov, Solution calorimetry of organic nonelectrolytes as a tool for investigation of intermolecular interactions, J. Phys. Org. Chem. 21 (2008) 2–13.

[21] B.N. Solomonov, A.I. Konovalov, V.B. Novikov, V.V. Gorbachuk, S.A. Neklyudov, Solvation of organic compounds determination of an enthalpy of the diluted substance specific interaction with a solvent, Zh. Obshch. Khim. 55 (1985) 1889–1906.

[22] B.N. Solomonov, A.I. Konovalov, V.B. Novikov, A.N. Vedernikov, M.D. Borisover, V.V. Gorbachuk, I.S. Antipin, Solvation of organic compounds. Molecular refraction, dipole moment and enthalpy of solution, Zh. Obshch. Khim. 54 (1984) 1622–1632.

[23] G.W. Wheland, D.E. Mann, The dipole moments of fulvene and azulene, J. Chem. Phys. 17 (1949) 264–268.

[24] R. Bramley, R.J.W. Le Fevre, Molecular polarisability. The anisotropies of diphenylpolyenes, J. Chem. Soc. (1960) 1820–1824.

[25] R.J.W. Le Fevre, A. Sundaram, K.M.S. Sundaram, Molecular polarisability. The molar Kerr constants and conformations of eight polyaryls as solutes, J. Chem. Soc. (1963) 3180–3187.

[26] K.J. Miller, Additivity methods in molecular polarizability, J. Am. Chem. Soc. 112 (1990) 8533–8542.

[27] F. Anger, R. Scholz, E. Adamski, K. Broch, A. Gerlach, Y. Sakamoto, T. Suzuki, Optical properties of fully and partially fluorinated rubrene in films and solution, Appl. Phys. Lett. 102 (2013) 013308.

[28] O.D. Jurchescu, A. Meetsma, T.T.M. Palstra, Low-temperature structure of rubrene single crystals grown by vapor transport, Acta Cryst. B 62 (2006) 330–334.

[29] M.A.A. Rocha, C.F.R.A.C. Lima, L.M.N.B.F. Santos, Phase transition thermodynamics of phenyl and biphenyl naphthalenes, J. Chem. Thermodyn. 40 (2008) 1458–1463.

[30] R.D. Chirico, W.V. Steele, A.F. Kazakov, Thermodynamic properties of 1-phenylnaphthalene and 2-phenylnaphthalene, J. Chem. Thermodyn. 73 (2014) 241–254.

[31] C.F.R.A.C. Lima, M.A.A. Rocha, B. Schröder, L.R. Gomes, J.N. Low, L.M.N.B.F. Santos, Phenylnaphthalenes: sublimation equilibrium, conjugation, and aromatic interactions, J. Phys. Chem. B 116 (2012) 3557–3570.

[32] C.F.R.A.C. Lima, M.A.A. Rocha, A. Melo, L.R. Gomes, J.N. Lowd, L.M.N.B.F. Santos, Structural and thermodynamic characterization of polyphenylbenzenes, J. Phys. Chem. A 115 (2011) 11876–11888.

[33] K.E. Maly, E. Gagnon, J.D. Wuest, Engineering molecular crystals with abnormally weak cohesion, Chem. Commun. 47 (2011) 5163–5165.

[34] J.S. Chickos, W.E. Acree, Enthalpies of sublimation of organic and organometallic compounds. 1910–2001, J. Phys. Chem. Ref. Data 31 (2002) 537–698.

[35] A. Bauder, H.H. Gunthard, Dampfdruck von azulen, Helv. Chim. Acta 45 (1962) 1698–1702.

[36] R.M. Stephenson, S. Malanowski, Handbook of the Thermodynamics of Organic Compounds, Elsevier, New York, 1987.

[37] J.S. Chickos, D. Hesse, S. Hosseini, G. Nichols, P. Webb, Sublimation enthalpies at 298.15 K using correlation gas chromatography and differential scanning calorimetry measurements, Thermochim. Acta 313 (1998) 10–110.

[38] E. Heilbronner, K. Wieland, Spektrographische und thermochemische untersuchungen an dampfförmigem azulen, Helv. Chim. Acta 30 (1947) 947–956.

[39] E. Morawetz, Enthalpies of vaporization for a number of aromatic compounds, J. Chem. Thermdyn. 4 (1972) 455–460.

[40] K.L. Wolf, H. Weghofer, Uber sublimationswarmen, Z. Phys. Chem. 39 (1938) 194–208.

[41] J.S. Chickos, R.S. Annunziata, L.H. Ladon, A.S. Hyman, J.F. Liebman, Estimating heats of sublimation of hydrocarbons. A semiempirical approach, J. Org Chem. 51 (1986) 4311–4314.

[42] H.P. Diogo, M.E. Minas da Piedade, A.C. Fernandes, J.A. Martinho Simoes, M.A.V. Riberio da Silva, M.J.S. Monte, The enthalpy of sublimation of diphenylacetylene from Knudsen effusion studies, Thermochim. Acta 228 (1993) 15–22.

[43] E.L. Eliel, J.J. Engelsman, The heats of combustion of gaseous cyclotetradecane and trans-stilbene – a tale of long-standing confusion, J. Chem. Educ. 73 (1996) 903–905.

[44] C.G. De Kruif, H.A.J. Oonk, The determination of enthalpies of sublimation by means of thermal conductivity manometers, Chem. Ing. Techn. 45 (1973) 455–461.

[45] P.J. Van Ekeren, M.H.G. Jacobs, J.C.A. Offringa, C.G. DeKruif, Vapour-pressure measurements on trans-diphenylethene and naphthalene using a spinning-rotor friction gauge, J. Chem. Thermodyn. 15 (1983) 409–417.

[46] G. Kratt, H.D. Beckhaus, W. Bernlöhr, C. Rüchardt, Thermolabile kohlenwasserstoffe XVII. Verbrennungsenthalpie und bildungsenthalpie von zehn sym.-tetraalkyl-1,2-diarylethanen, Thermochimica Acta 62 (1983) 279–294.

[47] H.K. Cammenga, H.J. Petrick, F.W. Schulze, Sublimation kinetics of organic molecular crystals, J. Cryst. Growth 55 (1981) 351–362.

[48] H.K. Cammenga, V.N. Emel, 'yanenko, S.P. Verevkin, Re-investigation and data assessment of the isomerization and 2,2'-cyclization of stilbenes and azobenzenes, Ind. Eng. Chem. Res. 48 (2009) 10120–10128.

[49] K. Nass, D. Lenoir, A. Kettrup, Calculation of the thermodynamic properties of polycyclic aromatic hydrocarbons by an incremental procedure, Angew. Chem. Int. Ed. Engl. 34 (1995) 1735–1736.

[50] R.S. Bradley, T.G. Cleasby, The vapour pressure and lattice energy of some aromatic ring compounds, J. Chem. Soc. (1953) 1690–1692.

[51] L. Malaspina, G. Bardi, R. Gigli, Simultaneous determination by Knudsen-effusion microcalorimetric technique of the vapor pressure and enthalpy of vaporization of pyrene and 1,3,5-triphenylbenzene, J. Chem. Thermodyn. 6 (1974) 1053–1064.

[52] N.K. Smith, R.C. Stewart Jr., A.G. Osborn, D.W. Scott, Pyrene: vapor pressure, enthalpy of combustion, and chemical thermodynamic properties, J. Chem. Thermodyn. 12 (1980) 919–926.

[53] K. Sasse, J. Jose, J.C. Merlin, A static apparatus for measurement of low vapor pressures. Experimental results on high molecular weight hydrocarbons, Fluid Phase Equilib. 42 (1988) 287–304.

[54] S. Yi, P. Ma, Y. Ruan, Determination of very low vapor pressures of seven organic compounds, J. Chem. Ind. and Eng. (China) 45 (1994) 102–105http://www.hgxb.com.cn/EN/.

[55] V. Oja, E.M. Suuberg, Measurements of the vapor pressures of coal tars using the nonisothermal Knudsen effusion method, J. Chem. Eng. Data 43 (1998) 486–492.

[56] H. Inokuchi, S. Shiba, T. Handa, H. Akamatu, Heats of sublimation le condensed polynuclear aromatic hydrocarbons, Bull. Chem. Soc. Jpn. 25 (1952) 299–302.

[57] W.J. Sonnefeld, W.H. Zoller, W.E. May, Dynamic coupled-column liquid chromatographic determination of ambient temperature vapor pressures of polynuclear aromatic hydrocarbons, Anal. Chem. 55 (1983) 275–280.

[58] J.L. Goldfarb, E.M. Suuberg, Vapor pressures and enthalpies of sublimation of ten polycyclic aromatic hydrocarbons determined via the Knudsen effusion method, J. Chem. Eng. Data 53 (2008) 670–676.

[59] K. Ruzicka, I. Mokbel, V. Majer, V. Ruzicka, J. Jose, M. Zabransky, Description of vapour-liquid and vapour–solid equilibria for a group of polycondensed compounds of petroleum interest, Fluid Phase Equilib. 148 (1998) 107–137.

[60] M.A. Siddiqi, R.A. Siddiqui, B. Atakan, Thermal stability, sublimation pressures, and diffusion coefficients of anthracene, pyrene, and some metal β-diketonates, J. Chem. Eng. Data 54 (2009) 2795–2802.

[61] R.H. Boyd, R.L. Christensen, R. Pua, The heats of combustion of acenaphthene, acenaphthylene, and fluoranthene. Strain and delocalization in bridged naphthalenes, J. Am. Chem. Soc. 87 (1965) 3554–3559.

[62] H. Yamasaki, K. Kuwata, Y. Kuge, Determination of vapor pressure of polycyclic aromatic hydrocarbons in the supercooled liquid phase and their adsorptiononairborne particulate matter, Nippon Kagaku Kaishi 8 (1984) 1324–1329.

[63] Y.D. Lei, R. Chankalal, A. Chan, F. Wania, Supercooled liquid vapor pressures of the polycyclic aromatic hydrocarbons, J. Chem. Eng. Data 47 (2002) 801–806.

[64] J.J.H. Haftka, J.R. Parsons, H.A.J. Govers, Supercooled liquid vapour pressures and related thermodynamic properties of polycyclic aromatic hydrocarbons determined by gas chromatography, J. Chromatogr. A 1135 (2006) 91–100.

[65] K. Sasse, J. N, 'Guimbi, J. Jose, J.C. Merlin, Tension de vapeur d'hydrocarbures polyaromatiques dans le domaine 10-3-10 Torr, Thermochim. Acta 146 (1989) 53–61.

[66] M.A.V. Ribeiro da Silva, L.M.N.B.F. Santos, L.M.S.S. Lima, Standard molar enthalpies of formation and of sublimation of the terphenyl isomers, J. Chem. Thermodyn. 40 (2008) 375–385.

[67] S.P. Verevkin, Thermochemistry of substituted benzenes. Experimental standard molar enthalpies of formation of o-, m-, and p-terphenyls and 1,3,5-triphenylbenzene, J. Chem. Thermodyn. 29 (1997) 1495–1501.

[68] N. Wakayama, H. Inokuchi, Heats of sublimation of polycyclic aromatic hydrocarbons and their molecular packings, Bull. Chem. Soc. Jpn. 40 (1967) 2267–2271.

[69] W. Hanshaw, M. Nutt, J.S. Chickos, Hypothetical thermodynamic properties. Subcooled vaporization enthalpies and vapor pressures of polyaromatic hydrocarbons, J. Chem. Eng. Data 53 (2008) 1903–1913.

[70] J.D. Kelley, F.O. Rice, The vapor pressures of some polynuclear aromatic hydrocarbons, J. Phys. Chem. 68 (1964) 3794–3796.

[71] D. Ferro, P. Imperatori, C. Quagliata, Study of the stability of the phenanthrene- and 1,2-benzanthracene-choleic acids by vapor pressure measurements, J. Chem. Eng. Data 28 (1983) 242–244.

[72] J.J. Murray, R.F. Pottie, C. Pupp, The vapor pressures and enthalpies of sublimation of five polycyclic aromatic hydrocarbons, Can. J. Chem. 52 (1974) 557.

[73] C.G. De Kruif, Enthalpies of sublimation and vapour pressures of 11 polycyclic hydrocarbons, J. Chem. Thermodyn. 12 (1980) 243–248.

[74] V.P. Klochkov, Davlenie nasyschennyh parov nekotoryh aromaticheskih soedinenii, Zh. Fiz. Khim. 32 (1958) 1177–1181.

[75] C.F. Shieh, N.W. Gregory, Vaporization characteristics of 9-phenylanthracene, J. Chem. Eng. Data 10 (1974) 11–14.

[76] M.A.V. Ribeiro da Silva, L.M.N.B.F. Santos, L.M.S.S. Lima, Thermodynamic study of 1,2,3-triphenylbenzene and 1,3,5-triphenylbenzene, J. Chem. Thermodyn. 42 (2010) 134–139.

[77] B. Stevens, Vapour pressures and the heats of sublimation of anthracene and of 9,10-diphenylanthracene, J. Chem. Soc. 76 (1953) 2973–2974.