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Measurement of the enthalpies of vaporization and sublimation of solids aromatic hydrocarbons by differential scanning calorimetry

Aarón Rojas*, Eulogio Orozco

Departamento de Química del Centro de Investigación y de Estudios Avanzados del I.P.N., Av. Instituto Politécnico Nacional 2508,
Col. San Pedro Zacatenco, México D.F., C.P. 07360, Mexico

Abstract

An experimental procedure is proposed for direct measurement of the heat involved in the vaporization of a solid organic compound above its normal melting temperature. This technique consists on the fusion of a solid aromatic hydrocarbon, which is then vaporized by a sudden decrease of the pressure. The direct register of heat flow as function of time by differential scanning calorimetry allows the quantifying of the enthalpy of vaporization of compounds such as phenanthrene, β-naphthol, pyrene, and anthracene. Enthalpies of vaporization were measured in an isothermal mode over a range of temperatures from 10 to 20 K above the melting temperatures of each compound, while enthalpies of fusion were determined from separate experiments performed in a scanning mode. Enthalpies of sublimation are computed from results of fusion and vaporization, and then compared with results from the literature, which currently are obtained by calorimetric or indirect techniques.

Keywords: Enthalpy of vaporization; Enthalpy of sublimation; Differential scanning calorimetry; β-Naphthol; Phenanthrene; Pyrene; Anthracene

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1. Introduction

Experimental evaluation of thermochemical properties of organic compounds in the gas phase requires determination of vaporization or sublimation enthalpies. There is a great variety of methods to quantify these properties. The currently utilized methods require considerable time and are in general indirect, based on the measurement of vapor pressures or mass effusion as a function of temperature. For substance with a high vapor pressure, sublimation or vaporization process can be performed without problems at relatively low temperatures. On the other hand, low volatility and technical problems inherent in measurement of the enthalpy of sublimation of a wide variety of solid aromatic hydrocarbons have been reported [1,2]. Therefore, reliable measurement of enthalpies of sublimation and vaporization of these compounds should be carried out at high temperatures even surpassing the melting point of the substance [3–6]. All these studies involve the design and construction of an experimental system able to support and work in a truthful way at those temperatures. Currently, direct measurement of the enthalpy of the sublimation or vaporization is done using a Calvet-type microcalorimeter [3,4,7–9], which is not always an available equipment in thermochemistry research laboratories.

Differential scanning calorimetry has been an important tool for the study of the thermal behavior and phase transitions of organic and inorganic substances. Carrying out adequate modifications, a scanning calorimeter can also be developed as an experimental

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* Corresponding author. Fax: +52-57-477113.
E-mail address: arojas@mail.cinvestav.mx (A. Rojas).

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instrument able to measure directly the heat transfer involved in the liquid–gas or solid–gas phase transitions of organic substances [10–15], at temperatures even above 500 K.

In this work, we describe a method for isothermal measurements of enthalpies of vaporization of the following aromatic compounds: β-naphthol, phenanthrene, pyrene, and anthracene above their fusion temperatures using a modified version of a differential scanning calorimeter DSC7. These modifications allow getting residual pressures of 15 Pa in a short time and an easy vaporization of melted aromatic compounds. This technique allows holding a constant pressure inside of the system throughout the vaporization experiment. Specific corrections of loss of mass caused by thermal equilibration, melting, and for a sudden decrease of pressure before vaporization are applied.

Development of this methodology shows that computation of the enthalpy of vaporization or sublimation at the reference temperature, requires of enthalpy of fusion, and heat capacities of the solid and liquid phases, therefore these quantities are also measured. A comparison of the results in relation to previously reported values of enthalpies of sublimation is also presented.

2. Experimental

The substances used in this work were phenanthrene, β-naphtol, pyrene, and anthracene; all of them commercial samples from J.T. Baker. These compounds were selected because they are very stable, most of their thermochemical properties are well defined and their normal fusion temperatures are around 360–490 K. All the substances were purified by repeated sublimation under vacuum at a residual pressure around of 20 Pa.

Experiments of fusion were performed in a Perkin Elmer DSC7 calorimeter. Measurements were done with a scanning rate from 0.0833 to 0.1667 $\mathrm{K\,s^{-1}}$, with samples of 2–5 mg inside of volatile sample pans. Each melting curve allowed computing the enthalpy and temperature of fusion and the purity of the sample was determined from a Van't Hoff graphic. Table 1 displays the experimental data and results of melting experiments for each compound. There, the uncertainty associated to each result represents once the standard deviation.

From this set of experiments, the mole fraction purity found for each substance was $x = (0.9997 \pm 0.0001)$ for phenanthrene, $x = (0.9994 \pm 0.0002)$ for β-naphtol, $x = (0.9996 \pm 0.0003)$ for pyrene, and $x = (0.9995 \pm 0.0003)$ for anthracene. Because the vaporization was done above the melting point of each substance and, to verify the stability of each compound during melting, a second scan was performed for each sample. A slight decomposition was denoted by a decrease of 0.003 with respect to the first observed mole fraction, but normally each sample maintained its purity after fusion.

The calorimetric measurements of enthalpies of vaporization were performed using the isothermal mode of the DSC7 calorimeter. For this type of determinations, a modification of the commercial apparatus was necessary. The experimental system and procedure have been already described [15] and only some details will be provided to understand the basic operating principle. The sensitive element of our device is a DSC7 calorimetric holder assembly (0319–0006, Perkin Elmer), which was placed into a vacuum chamber assembled from a measurement piece (DN100 ISO K, Balzers), as shown in Fig. 1. A heat exchanger, made in copper and aluminum, connected to a constant temperature recirculation bath (RM6 Lauda, Brinkmann) allows the temperature regulation of the entire calorimetric holder. In the top of the vacuum chamber a cold trap is assembled to condense most of the vaporized substance avoiding condensation around the sensitive element. With this, some inaccuracies previously observed by other authors in phase change calorimetric techniques [3,11] are eliminated. The calorimetric holder assembly is connected to the DSC7 control device using an electrical feedthrough. The vaporization system is evacuated with a rotary vane pump and, residual pressure inside of the chamber is monitored by a pressure gauge, which is relayed to a Pirani gauge control Thermovac TM20 from Leybold. A set of three valves between the sublimation system and the rotary vane pump, allows the evacuation of the sublimation chamber and good control of the residual pressure. The latter remains constant throughout the vaporization process. The calorimetric assembly, the vacuum chamber, and all the accessories of the vaporization system are autonomous and

Table 1
Temperatures, enthalpies, and purity resulting from the fusion experiments

m_{sample} (mg)	Scanning rate (K s^{-1})	Purity (mole fraction)	T_{fus} (K)	$\Delta_{\text{fus}}H(T_{\text{fus}})$ (kJ mol^{-1})
β-Naphtol, scanning range: 363.15–413.15 K				
2.046	0.0833	0.9992	392.48	21.20
3.668	0.0833	0.9992	392.68	20.81
3.794	0.0833	0.9994	392.90	21.10
3.393	0.0833	0.9997	392.52	20.58
3.673	0.0833	0.9996	392.26	20.84
3.518	0.0833	0.9994	392.41	20.71
		(0.9994 ± 0.0002)	(392.54 ± 0.22)	(20.87 ± 0.23)
Phenantrene, scanning range: 353.15–383.15 K				
1.012	0.1667	0.9996	367.70	16.39
2.577	0.1667	0.9998	367.68	16.63
2.818	0.1667	0.9995	368.00	16.64
2.909	0.1667	0.9996	367.75	16.54
2.175	0.1667	0.9998	367.50	16.58
2.047	0.1667	0.9999	367.32	16.60
1.998	0.1667	0.9996	366.90	16.61
		(0.9997 ± 0.0001)	(367.55 ± 0.36)	(16.57 ± 0.09)
Pyrene, scanning range: 403.15–433.15 K				
3.330	0.0833	0.9998	423.00	16.46
2.170	0.0833	0.9995	422.36	16.17
3.271	0.0833	0.9998	422.15	16.68
3.161	0.0833	0.9990	422.17	17.59
3.376	0.0833	0.9998	422.19	16.51
		(0.9996 ± 0.0003)	(422.37 ± 0.36)	(16.68 ± 0.54)
Anthracene, scanning range: 463.15–503.15 K				
1.841	0.1667	0.9997	489.97	29.21
3.248	0.1667	0.9991	491.83	29.79
5.152	0.1667	0.9995	492.46	30.20
4.818	0.1667	0.9997	492.96	30.35
3.646	0.1667	0.9997	492.68	29.67
		(0.9995 ± 0.0003)	(491.98 ± 1.20)	(29.84 ± 0.45)

all other normal function of the DSC7 device can work independently of the described modifications.

The commercial pans for volatile samples (Perkin Elmer, 0219–0062) were utilized as vaporization cells, but previously were modified making a hole with a drill of diameter 0.3 mm. After drilling, the edge of the hole was sanded with a fine sanding film. This vaporization hole was chosen as most suitable because larger diameters cause a quick vaporization with a time of the experiment too short to reach a good register of transferred heat.

From preliminary experiments, the working temperatures for the vaporization were established around 10–20 K above the normal melting temperature of each substance. This set of experiments was also useful to verify the range of the calorimetric signal and the time for the total vaporization of each compound. This information and the mass of the sample are required for the isothermal operation of the DSC7 calorimeter.

In a typical vaporization experiment, an empty pan for vaporization is weighed; then around 5 mg of the solid substance is placed inside and the pan is sealed using a pan sealer (Perkin Elmer 219–0061). The pans and samples were weighed on a Sartorius 4503 microbalance, sensitive to 1 μg (inaccuracy ±1 μg). The

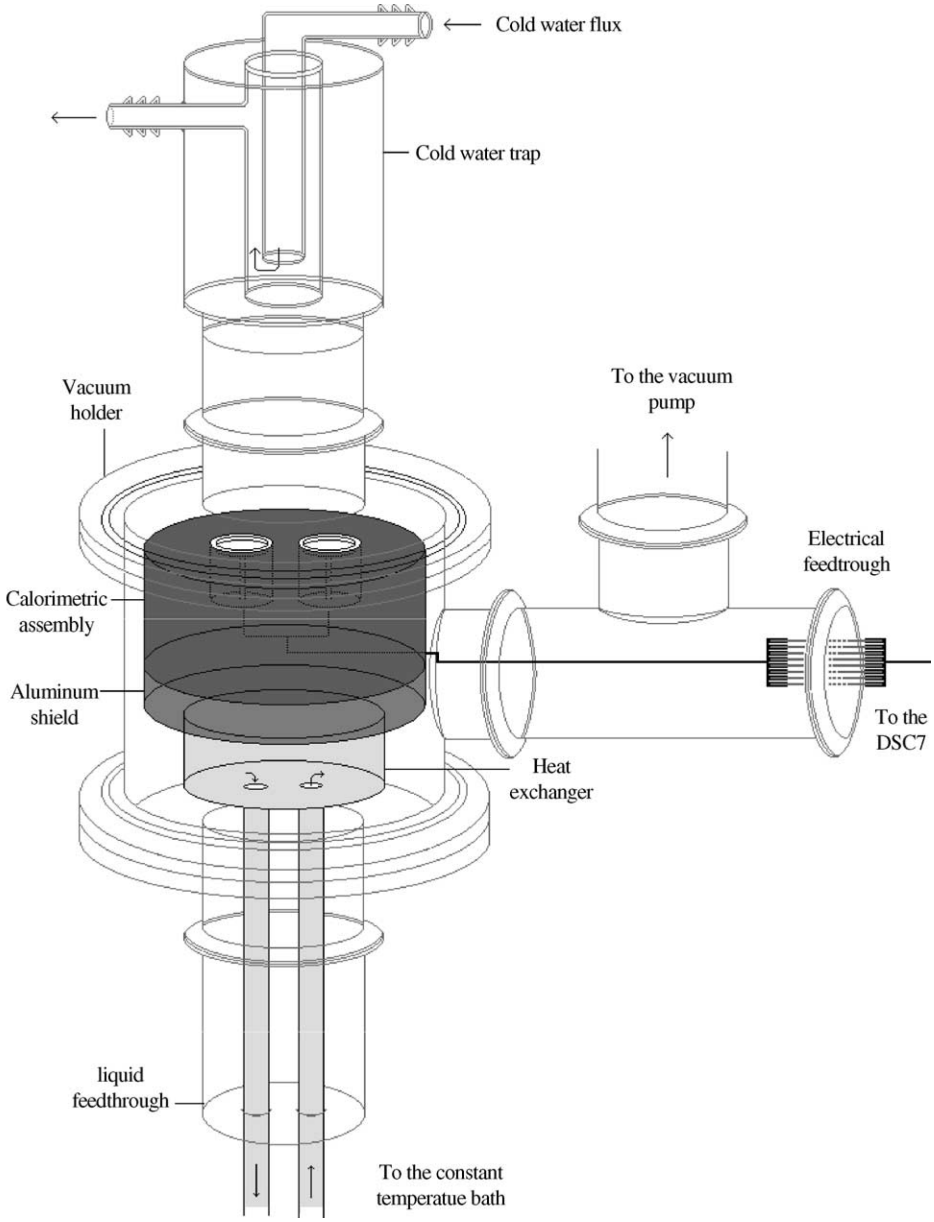

Fig. 1. Experimental device.

pan is then loaded in the sample holder and an identical but empty vaporization pan is loaded in the reference holder. Once inside the calorimetric system, by the direct temperature control of the calorimetric holders, the sample is slowly heated 10 K above its melting temperature. At this point, temperature and heat flux are stabilized and data acquisition begins. Five minutes are enough to get a good initial baseline, then the valve connected to the vacuum pump is opened, the pressure inside the vacuum chamber is downloaded quickly and the vaporization process of the melted compound begins.

Residual pressure is an important variable in the vaporization process of the melted compound; this parameter is controlled by regulation of the set of valves of the vacuum system, getting a constant pressure in the range 5–15 Pa, throughout the vaporization process. The substances studied have a relatively high vapor pressure once they are melted, therefore a good selection of the residual pressure allows control of the rate of vaporization. Long and flat curves are preferred, because this is an insight that vaporization occurs approaching the equilibrium conditions. Typical profiles of the calorimetric curves are shown in Fig. 2 and are related to the diameter of the vaporization hole, the experimental temperature, the time of total vaporization, and the initial mass of the substance.

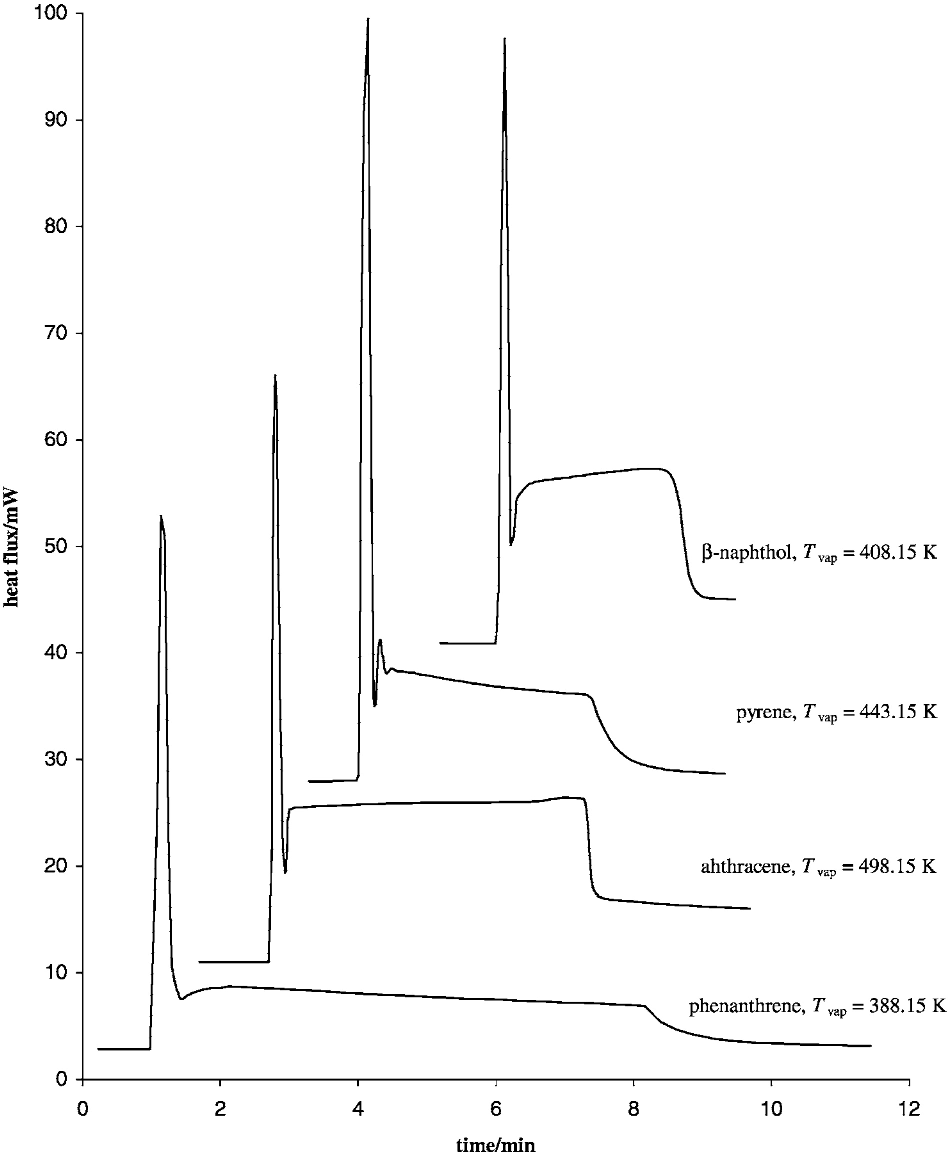

Fig. 2. Profile of the curves of vaporization for each aromatic hydrocarbon.

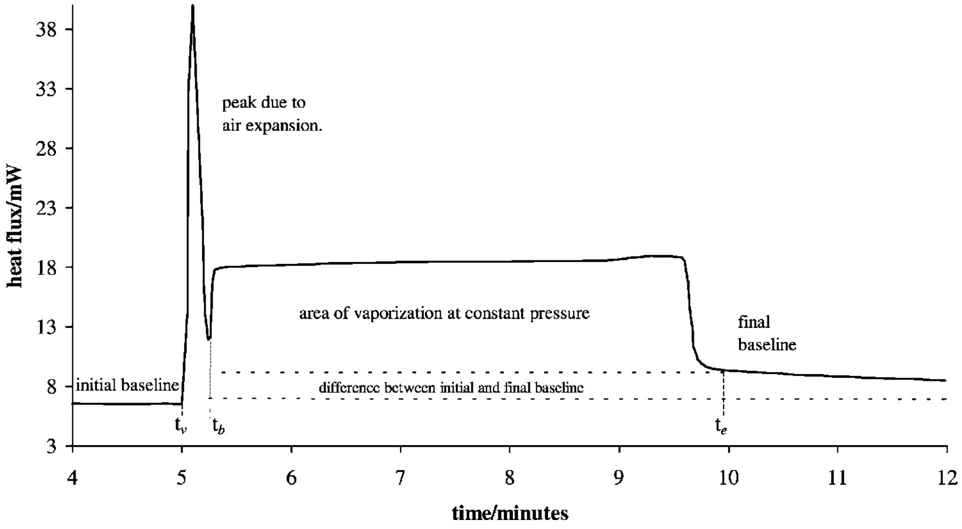

Fig. 3. Detailed vaporization curve for anthracene. The sharpened peak after initial base line is due to evacuation pumping, which is started at the time t_v. Loss of mass in condition of no equilibrium is quantified by independent experiments in the interval involving loading of the sample, melting, thermal stabilization, and initial vacuum pumping, it means from the weighing of the sample until the time t_b. Vaporization approaching conditions of equilibrium at constant pressure begins at time t_b, and ends at time t_0.

A detailed calorimetric vaporization curve is shown in Fig. 3. The sharpened peak shown as vacuum pumping peak on this figure is produced by the expansion of residual air when the vacuum pump valve is opened and is due to a sudden pressure change inside of the chamber. Conditions of constant pressure in the system are attained just at the time t_b, where a slow vaporization of the sample with equilibrium between gas and solid phases begins. This equilibrium is denoted as a plateau in the profile of the curve of vaporization. Once the substance is evaporated, the calorimetric signal returns to baseline and, at the time t_e, the vaporization process is considered finished. Below the curve of vaporization, there is a zone due to the difference between the initial and final baseline. This is consequence of some asymmetry and different heat capacities of the full and empty sample pan; however, this difference in most of the cases is less than 1 mW.

During the loading of the sample, melting, thermal stabilization, and pressure change due to initial pumping, a small fraction of the substance vaporizes before the change of phase in conditions of equilibrium. In consequence, an exact result of the enthalpy of vaporization requires the quantification of mass lost in that interval and it was performed by independent experiments. In this set of experiments, a vaporization pan was also charged with around 5 mg of each compound and was positioned in the sensor holder. The substance was melted and stabilized, and the vacuum chamber was evacuated as in a vaporization experiment, but after air evacuation and before the slow vaporization process at constant pressure (point t_b in Fig. 3), the experiment was stopped by suddenly decreasing the temperature and breaking the vacuum. Immediately the sample was reweighed and mass lost due to the loading, melting, thermal stabilization, and vacuum pumping was computed. Results of these experiments for each compound are reported in Table 2. There, the uncertainty associated to the result of mass lost represent the standard deviation.

Once the mass lost in conditions of no equilibrium was quantified, the calculation of vaporization enthalpy involves only the slow process of vaporization between the time of beginning (t_b) and end (t_e) of the curve in Fig. 3, identified as the vaporization at constant pressure area. This zone was evaluated using a numerical method and represents the heat transferred per mass unit during the vaporization process approaching the conditions of equilibrium between the solid and gas phase. Knowing the initial mass, the mass lost before the vaporization at constant pressure, and the area of the measured curve, the vaporization

Table 2
Mass lost during fusion, thermal stabilization, and air expansion in vaporization experiments

Initial mass (mg)	Final mass (mg)	Mass lost (mg)	Mass lost (%)
β-Naphtol			
6.232	5.801	0.431	6.92
5.801	5.407	0.394	6.79
6.077	5.588	0.489	8.05
5.589	5.135	0.454	8.12
5.087	4.63	0.457	8.98
6.916	6.501	0.415	6.00
6.5	6.016	0.484	7.45
6.615	6.073	0.542	8.19
6.327	5.98	0.347	5.48
5.97	5.565	0.405	6.78
			(7.28 ± 1.08)
Phenantrene			
6.184	5.815	0.369	5.97
6.676	6.285	0.391	5.86
6.285	5.944	0.341	5.43
7.135	6.802	0.333	4.67
5.223	4.929	0.294	5.63
4.929	4.634	0.295	5.98
4.499	4.21	0.289	6.42
4.968	4.767	0.201	4.05
5.146	4.821	0.325	6.32
4.821	4.54	0.281	5.83
5.498	5.21	0.288	5.24
5.21	4.925	0.285	5.47
			(5.57 ± 0.68)
Pyrene			
4.261	3.965	0.296	6.95
6.823	6.277	0.546	8.00
6.03	5.692	0.338	5.61
5.397	4.986	0.411	7.62
6.932	6.532	0.4	5.77
7.008	6.576	0.432	6.16
6.309	5.83	0.479	7.59
6.552	6.126	0.426	6.50
6.94	6.512	0.428	6.17
7.243	6.842	0.401	5.54
			(6.59 ± 0.90)
Anthracene			
7.102	6.663	0.439	6.18
6.854	6.421	0.433	6.32
6.532	6.108	0.424	6.49
5.896	5.533	0.363	6.16
6.317	5.907	0.41	6.49
5.967	5.589	0.378	6.33
6.123	5.711	0.412	6.73
6.511	6.098	0.413	6.34
			(6.38 ± 0.19)

heat was obtained using the relation:

$$Q_{\mathrm{vap}} = \frac{\text{constant pressure vaporization area (W s)}}{\text{initial mass (g)} - \text{mass lost (g)}} \quad (1)$$

where *initial mass* is the mass of the sample recorded in the weighing and *mass lost* is the mass of the sample evaporated in conditions of no equilibrium.

On the other hand, heat capacities of each solid and liquid aromatic hydrocarbon were also measured by differential scanning calorimetry, but using the commercial version of the DSC7. Due to the reduced mass of samples and therefore the small quantities of heat involved in the heat capacity measurements, additional care was taken, especially with melted samples. The chosen scanning rate for this purpose was $3.33 \times 10^{-3}\,\mathrm{K\,s^{-1}}$. The reliability of the results was tested by the measurement of heat capacity of saphire in the range of room temperature to 395 K. For this substance we found $c_{p,\mathrm{m}}$ (298.15 K) = (79.59 ± 1.89) $\mathrm{J\,K^{-1}\,mol^{-1}}$ and $c_{p,\mathrm{m}}$ (395 K) = (96.36 ± 2.13) $\mathrm{J\,K^{-1}\,mol^{-1}}$, in good agreement with the values recommended in this Journal [16].

Currently the calorimetric holder assembly inside of the vacuum system and that of the commercial DCS7 are calibrated for energy and temperature using high-purity samples of indium and zinc at scanning rate of $0.0667\,\mathrm{K\,s^{-1}}$.

3. Results and discussion

Table 3 shows the experimental values and the resulting enthalpies of vaporization for each compound studied. The mean value for the enthalpy of vaporization was obtained at the working temperature with at least five experiments. The associated uncertainties represent the standard deviation. Integration of the area of the calorimetric curve was done using a numerical data treatment software Microcal Origin version 4.00. A sublimation hole of diameter 0.3 mm was found adequate for all the experiments. From the time of the experiment and mass of the sample vaporized at constant pressure, the average vaporization speed for each compound can be calculated as 3×10^{-5} and $1 \times 10^{-5}\,\mathrm{g\,s^{-1}}$ for β-naphthol and phenanthrene,

Table 3
Experiments of vaporization of the aromatic hydrocarbons[a]

m_{initial} (mg)	m_{lost} (mg)	$m_{\text{vaporized}}$ (mg)	t (s)	S (mW s^{-1})	Q_{vap} (J g^{-1})	$\Delta_{\text{vap}}H(T)$ (kJ mol^{-1})
β-Naphtol, $T_{\text{vap}} = 408.15$ K						
5.298	0.386	4.912	182	2047.611	416.82	60.09
5.303	0.386	4.917	193	2042.313	415.35	59.88
5.744	0.418	5.326	165	2178.567	409.04	58.97
6.533	0.475	6.058	188	2494.602	411.81	59.37
4.876	0.355	4.521	134	1811.61	400.70	57.77
5.641	0.410	5.231	155	2113.155	404.01	58.25
5.363	0.390	4.973	179	2018.829	405.98	58.53
5.302	0.386	4.916	206	2062.491	419.53	60.48
5.194	0.378	4.816	201	2047.158	425.07	61.28
						(59.40 ± 1.14)
Phenantrene, $T_{\text{vap}} = 388.15$ K						
5.920	0.330	5.590	598	2195.121	392.67	69.99
6.788	0.378	6.410	643	2483.823	387.50	69.06
4.515	0.252	4.263	570	1663.515	390.18	69.54
5.146	0.287	4.859	505	1866.375	384.08	68.46
5.002	0.279	4.723	523	1827.849	386.98	68.97
5.441	0.303	5.138	634	1977.939	384.97	68.61
5.218	0.291	4.927	530	1918.002	389.26	69.38
5.4	0.301	5.099	600	1971.387	386.61	68.91
4.921	0.274	4.647	574	1805.433	388.53	69.25
5.305	0.296	5.009	628	1885.452	376.38	67.08
						(68.92 ± 0.79)
Pyrene, $T_{\text{vap}} = 443.15$ K						
5.510	0.363	5.147	275	1700.751	330.44	66.83
6.077	0.400	5.677	330	1834.221	323.12	65.35
6.102	0.402	5.700	337	1827.621	320.64	64.85
6.869	0.453	6.416	310	2125.665	331.29	67.00
7.084	0.467	6.617	284	2163.777	326.99	66.14
6.737	0.444	6.293	326	2061.243	327.54	66.25
						(66.07 ± 0.84)
Anthracene, $T_{\text{vap}} = 498.15$ K						
6.297	0.402	5.895	186	2219.288	376.45	67.10
5.43	0.346	5.084	172	1908.957	375.52	66.93
4.781	0.305	4.476	226	1659.852	370.84	66.09
4.884	0.3116	4.572	214	1713.186	374.68	66.78
5.565	0.355	5.210	216	1943.244	372.99	66.48
						(66.68 ± 0.40)

[a] The diameter of the hole of vaporization was 0.3 mm for each experiment. In the head of column t is the time of the vaporization process and S is the area under the vaporization curve. To compute the enthalpy of vaporization in kJ mol^{-1}, the molar mass of each substance was calculated from the atomic weights recommended by the IUPAC [17] giving 144.170, 178.229, 202.250, and 178.229 g mol^{-1}, respectively for β-naphtol, phenanthrene, pyrene, and anthracene.

respectively, and around 2×10^{-5} g s^{-1} for pyrene and anthracene.

There are many paths to reach the gas phase from the condensed phase at the experimental temperature, however two of them, shown in Fig. 4, are interesting for us. This is because they involve experimentally measured quantities and the enthalpy of sublimation at the reference temperature.

Path I goes from the solid to the gas phase throughout heating and fusion of the solid, then heating and

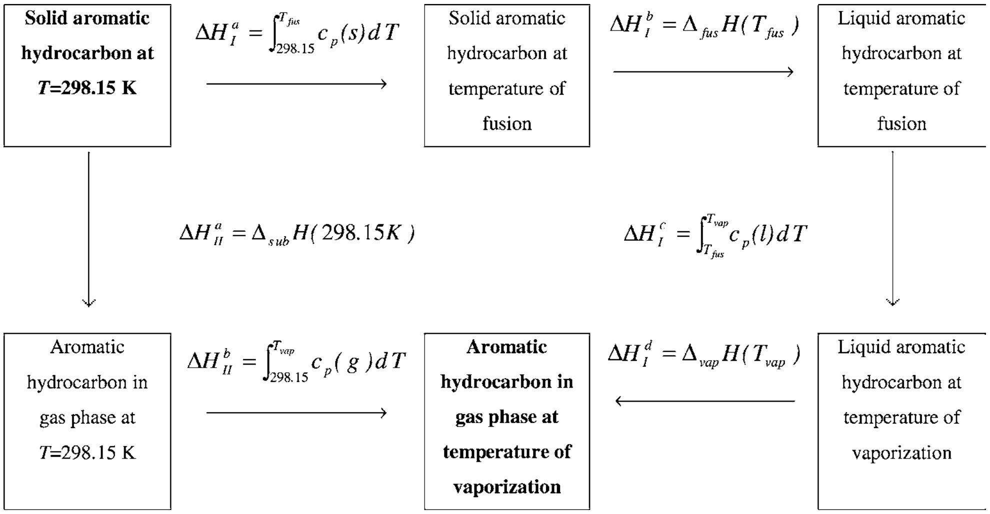

Fig. 4. Thermodynamics paths to compute the enthalpy of sublimation at the reference and experimental temperatures.

sudden vaporization of liquid, as was carried out experimentally. On the other hand, path II involves only the process of sublimation at the temperature of reference followed by heating of the gas phase until the experimental temperature of vaporization. From this scheme is evident that

$$\Delta H_{\mathrm{II}}^{\mathrm{a}} + \Delta H_{\mathrm{II}}^{\mathrm{b}} = \Delta H_{\mathrm{I}}^{\mathrm{a}} + \Delta H_{\mathrm{I}}^{\mathrm{b}} + \Delta H_{\mathrm{I}}^{\mathrm{c}} + \Delta H_{\mathrm{I}}^{\mathrm{d}} \quad (2)$$

Hence, the enthalpy of sublimation at 298.15 K ($\Delta H_{\mathrm{II}}^{\mathrm{a}}$) can be computed as

$$\begin{aligned} &\Delta_{\mathrm{sub}} H(298.15\,\mathrm{K}) \\ &\quad = \int_{298.15\,\mathrm{K}}^{T_{\mathrm{fus}}} c_p(\mathrm{s})\,\mathrm{d}T + \Delta_{\mathrm{fus}} H(T_{\mathrm{fus}}) \\ &\qquad + \int_{T_{\mathrm{fus}}}^{T_{\mathrm{vap}}} c_p(\mathrm{l})\,\mathrm{d}T + \Delta_{\mathrm{vap}} H(T_{\mathrm{vap}}) \\ &\qquad - \int_{298.15\,\mathrm{K}}^{T_{\mathrm{vap}}} c_p(\mathrm{g})\,\mathrm{d}T \qquad (3) \end{aligned}$$

where the heat capacities at constant pressure of solid, liquid, and gas are denoted by c_p(s), c_p(l), and c_p(g), respectively and are indispensable to determine $\Delta_{\mathrm{sub}} H$(298.15 K). Change of enthalpy for heating of condensed phases is restricted to compute the integral of c_p between temperatures because the process of heating is actually done at constant pressure. Change of enthalpy due to heating of the gas phase is computed in the same way, but under assumption that the substance in vapor phase behaves ideally.

Heat capacities of solid aromatic compounds were measured in a temperature range of 298.15, 10, or 20 K below the melting temperature. In the particular case of phenanthrene, the heat capacity of the solid was measured between 298.15 and 360 K, but data in the range 327–349 K are not reported due to a crystalline transformation in this interval. The enthalpy change for this process was measured from three experiments and an enthalpy of transformation between crystalline phases of $\Delta_{\mathrm{I} \to \mathrm{II}} H = (853.1 \pm 71.8)\,\mathrm{J\,mol^{-1}}$ was found at $T = (345.2 \pm 1.1)$ K.

For each melted compound, heat capacity was measured until 20 K above its melting temperature, it means, in the same interval of temperature as the vaporization experiments. For condensed phases, equations of the type $c_p = a + bT + cT^2$ were fitted to the experimental results. Correlation coefficients for the fitted curves were always greater than 0.97, except for liquid pyrene and anthracene, whose heat capacities were measured to higher temperatures than the other two compounds. Data of c_p for the gas phase were taken from reference [18] and were fitted as for the condensed phases, to a quadratic equation. All these heat capacity data are displayed in Table 4.

From the paths of the scheme given in Fig. 4, Eq. (3), and heat capacities as function of the temperature, the enthalpies of sublimation at 298.15 K were calculated and are reported in Table 6. For the particular case of phenanthrene, evaluation of the change

Table 4
Solid, liquid, and gas heat capacities at constant pressure of the four aromatic compounds studied

Solid β-naphthol		Liquid β-naphthol		Gaseous β-naphthol [18]	
T (K)	c_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	c_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	c_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
298.15	178.17 ± 1.85	397	294.86	50	37.44
300	181.35	398	297.13	100	53.10
305	186.57	399	297.24	150	73.93
310	189.65	400	300.28	200	98.14
315	192.16	401	300.73	273.15	136.34
320	195.81	402	301.15	298.15	149.44
325	198.35	403	302.27	300	150.40
330	200.88	404	303.41	400	199.15
335	202.91	405	303.54	500	239.47
340	205.46	406	304.68	600	271.50
345	208.52	407	305.53	700	297.01
350	209.48	408	305.61	800	317.66
355	213.09	408.15	305.70	900	334.68
360	217.24	409	306.06	1000	348.91
		410	306.56	1100	360.92
		411	307.03	1200	371.14
		412	306.83	1300	379.88
		413	307.31	1400	387.41
		414	307.72	1500	393.92
		415	307.84		
		416	307.92		
	c_p (β-naphthol, cr) $= -279.44 + 2.3473T - 2.7022 \times 10^{-3}T^2$		c_p (β-naphthol, l) $= -6083.4 + 30.793T - 3.7091 \times 10^{-2}T^2$		c_p (β-naphthol, g) $= 3.8296 + 0.54906T - 1.9737 \times 10^{-4}T^2$
Solid phenanthrene		Liquid phenanthrene		Gaseous phenanthrene [18]	
298	212.38	382	269.53	50	41.4
298.15	212.42 ± 0.97	383	274.57	100	62.2
299	216.51	384	286.02	150	88.7
300	219.35	385	291.05	200	119.6
301	222.17	386	296.10	273.15	168.7
302	225.03	387	301.11	298.15	185.7
303	227.21	388.15	310.17	300	186.9
304	230.05	389	304.69	400	250.4
305	231.55	390	316.13	500	303.4
306	233.06	391	311.53	600	345.8
307	235.23	392	310.15	700	379.6
308	234.76	393	315.17	800	407.1
309	236.93			900	429.6
310	239.11			1000	448.5
311	239.31			1100	464.3
312	240.82			1200	477.7
313	241.03			1300	489.1
314	243.19			1400	498.9
315	244.04			1500	507.3
316	247.56				
317	248.26				
318	249.27				
319	250.79				
320	252.33				
321	253.80				
322	255.33				

Table 4 (*Continued*)

Solid phenanthrene		Liquid phenanthrene		Gaseous phenanthrene [18]	
323	256.84				
324	258.38				
325	259.88				
326	262.04				
327	265.57				
349	276.38				
350	275.92				
351	274.15				
352	276.34				
353	275.87				
354	275.25				
355	274.89				
356	275.77				
357	277.30				
358	276.24				
359	276.43				
360	278.51				
	c_p (phenanthrene, cr) $= -2082.5 + 13.282T - 1.8696 \times 10^{-2}T^2$		c_p (phenanthrene, l) $= -66717 + 341.85T - 0.43586T^2$		c_p (phenanthrene, g) $= -3.2428 + 0.71536T - 2.5576 \times 10^{-4}T^2$
Solid pyrene		Liquid pyrene		Gaseous pyrene [18]	
298.15	234.86 ± 3.09	427	320.20	298.15	204.2
300	239.39	428	325.24	300	205.6
305	276.72	429	328.10	400	275.5
310	288.19	430	329.86	500	333.6
315	297.83	431	331.66	600	379.9
320	307.64	432	332.36	700	416.7
325	317.49	433	334.13	800	446.5
330	327.05	434	332.67	900	470.9
335	335.30	435	333.36	1000	491.1
340	341.46	436	334.04		
345	349.06	437	334.78		
350	356.43	438	333.26		
355	364.02	439	335.10		
360	370.68	440	335.74		
365	377.39	441	334.32		
370	383.16	442	334.97		
375	390.66	443	335.67		
380	391.60	443.15	334.70		
385	398.51				
390	404.77				
395	410.42				
400	414.46				
405	418.54				
410	420.17				
415	420.80				
	c_p (pyrene, cr) $= -1441.6 + 8.6970T - 1.0153 \times 10^{-2}T^2$		c_p (pyrene, l) $= -15931 + 74.089T - 8.4365 \times 10^{-2}T^2$		c_p (pyrene, g) $= -40.207 + 0.95261T - 4.2475 \times 10^{-4}T^2$

Table 4 (*Continued*)

Solid anthracene		Liquid anthracene		Gaseous anthracene [18]	
298.15	207.55 ± 1.27	495	400.92	50	41.38
300	211.69	496	417.43	100	61.44
305	216.52	497	423.66	150	87.8
310	219.32	498	424.76	200	118.55
315	223.08	498.15	419.80	273.15	167.75
320	225.56	499	425.97	298.15	184.74
325	227.36	500	432.20	300	185.99
330	228.42	501	438.47	400	249.74
335	230.87	502	429.34	500	302.9
340	231.92	503	425.39	600	345.39
345	233.97			700	379.33
350	236.47			800	406.84
355	237.60			900	429.48
360	237.95			1000	448.32
365	240.13			1100	464.17
370	239.74			1200	477.58
375	239.48			1300	489.01
380	240.24			1400	498.8
385	240.94			1500	507.22
390	240.03				
395	241.44				
400	240.47				
405	241.18				
410	240.57				
415	240.62				
420	241.41				
425	243.16				
430	243.82				
	c_p (anthracene, cr) $= -220.78 + 2.3113T - 2.8826 \times 10^{-3}T^2$		c_p (anthracene, l) $= -2.1831\times 10^5 + 873.77T - 0.87258T^2$		c_p (anthracene, g) $= -6.1453 + 0.71903T – 2.5690 \times 10^{-4}T^2$

of enthalpy associated with path I must also include the crystalline transition described above. Calculation of the enthalpy of sublimation at the experimental temperature can be deduced from a similar scheme of that shown in Fig. 4, but path II involve heating of the solid from the reference temperature to the vaporization temperature followed by the sublimation at this temperature. An expression to compute the enthalpy of sublimation of the compound at its temperature of vaporization is then derived as

$$\Delta_{\mathrm{sub}}H(T_{\mathrm{vap}}) = \int_{298.15}^{T_{\mathrm{fus}}} c_p(\mathrm{s})\,\mathrm{d}T + \Delta_{\mathrm{fus}}H(T_{\mathrm{fus}}) + \int_{T_{\mathrm{fus}}}^{T_{\mathrm{vap}}} c_p(\mathrm{l})\,\mathrm{d}T + \Delta_{\mathrm{vap}}H(T_{\mathrm{vap}}) - \int_{298.15}^{T_{\mathrm{vap}}} c_p(\mathrm{s})\,\mathrm{d}T \qquad (4)$$

Alternatively, enthalpy of melting can be carried at the temperature of vaporization and the enthalpy of sublimation at this experimental temperature can be computed as the sum $\Delta_{\mathrm{fus}}H(T_{\mathrm{vap}}) + \Delta_{\mathrm{vap}}H(T_{\mathrm{vap}})$. A summary of all the thermodynamics quantities measured and derived for the aromatic compounds studied in this work is displayed in Table 5.

Computation of the integrals $\int_{298.15}^{T_{\mathrm{fus}}} c_p(\mathrm{s})\,\mathrm{d}T$, $\int_{T_{\mathrm{fus}}}^{T_{\mathrm{vap}}} c_p(\mathrm{l})\,\mathrm{d}T$, and $\int_{298.15}^{T_{\mathrm{vap}}} c_p(\mathrm{g})\,\mathrm{d}T$ in Eqs. (3) and (4) is equivalent to determine the area under the curve $c_p(T)$, which is similar to a trapezoid. Error propagation associated with these quantities was then calculated applying specific formulas and procedures given in the reference [19], considering an uncertainty of $\pm 2.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$ in the measurement of the heat capacity, and $\pm 0.1\,\mathrm{K}$ in the measurement of temperature by the scanning calorimeter. The

Table 5
Summary of the measured thermodynamic quantities of the substances studied in this work

	β-Naphthol	Phenantrene	Pyrene	Anthracene
C_p (cr, 298.15 K) ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	178.17 ± 1.85	212.42 ± 0.97	234.86 ± 3.09	207.55 ± 1.27
$\Delta_{\mathrm{fus}}H(T_{\mathrm{fus}})$ ($\mathrm{kJ\,mol^{-1}}$)	20.87 ± 0.23	16.57 ± 0.09	16.68 ± 0.54	29.84 ± 0.45
$\Delta_{\mathrm{fus}}H(T_{\mathrm{vap}})$ ($\mathrm{kJ\,mol^{-1}}$)	21.99 ± 0.24	15.36 ± 0.11	14.78 ± 0.55	30.97 ± 0.46
$\Delta_{\mathrm{vap}}H(T_{\mathrm{vap}})$ ($\mathrm{kJ\,mol^{-1}}$)	59.40 ± 1.14	68.92 ± 0.79	66.07 ± 0.84	66.67 ± 0.40
$\Delta_{\mathrm{sub}}H(T_{\mathrm{vap}})$ ($\mathrm{kJ\,mol^{-1}}$)	81.40 ± 1.17	84.28 ± 0.80	80.85 ± 1.00	97.65 ± 0.61
$\Delta_{\mathrm{sub}}H(298.15\,\mathrm{K})$ ($\mathrm{kJ\,mol^{-1}}$)	85.53 ± 1.18	89.57 ± 0.81	98.49 ± 1.04	96.31 ± 0.72

resulting uncertainties associated with those integrals were from $0.05\,\mathrm{kJ\,mol^{-1}}$ for the heating of the liquid to $0.20\,\mathrm{kJ\,mol^{-1}}$ for the heating of the gas. The uncertainty in the result of enthalpy of sublimation at 298.15 K, reported in Table 5, includes these results and the experimental uncertainty of melting and vaporization experiments.

There are very few works reporting the change of enthalpy associated with the change liquid phase → gas phase for the aromatic compounds studied in this work [3,4]. On the other hand, enthalpy of sublimation is the currently measured quantity for phase change condensed phase → gas phase and consequently there are enough values in the literature to compare. This comparison is given in Table 6.

In Table 6, we have selected only the most representative techniques and works, some literature data are not considered there, have been previously reviewed and included or discarded in the analysis of reference materials performed by Sabbah and coworkers and published in this Journal [16]. This revision is introduced in Table 6 as the recommended value.

Uncertainty related to previous calorimetric measurements of $\Delta_{\mathrm{sub}}H(T)$ shown in Table 6 is in general the standard deviation. For measurements of vapor pressure or mass effusion, the uncertainty is that associated to the least squares fitting. To get a reliable comparison between the values reported by different authors, when the enthalpy of sublimation at 298.15 K was not reported in the original work, it was calculated from the experimental value using the equation:

$$\Delta_{\mathrm{sub}}H(298.15\,\mathrm{K}) = \Delta_{\mathrm{sub}}H(T_{\mathrm{sub}}) - \int_{298.15\,\mathrm{K}}^{T_{\mathrm{sub}}} \Delta_{\mathrm{sub}}c_{p,\mathrm{m}}\,\mathrm{d}T \qquad (5)$$

where the value of $\Delta_{\mathrm{sub}}c_{p,\mathrm{m}}$ for each sublimation process was calculated from data of heat capacity of the solid phase at 298.15 K and the gas phase at 300 K, all of them displayed in Table 4.

Values of enthalpy of sublimation of β-naphthol are spread between 76.1 and $94.7\,\mathrm{kJ\,mol^{-1}}$ all them measured by indirect methods, no calorimetric measurement has been performed for this substance and, a recommended value has not been proposed. However, the result of $(85.53 \pm 1.18)\,\mathrm{kJ\,mol^{-1}}$ obtained in this work by DSC is very near of the midpoint of the range of those previously reported results for this compound. For phenanthrene direct calorimetric measurements of the enthalpy of sublimation were achieved by Morawetz using a Calvet calorimeter [3] and, by Torres-Gómez using isothermal DSC [14], the result of $\Delta_{\mathrm{sub}}H(298.15\,\mathrm{K}) = (89.57 \pm 0.81)\,\mathrm{kJ\,mol^{-1}}$ provided in the current work, presents a good agreement with their result and with the recommended value [16]. Enthalpy of sublimation for the pyrene has been also measured using calorimetric or indirect methods, with a good agreement between all values, included that obtained in this work. Finally, for this set of aromatic compounds, anthracene has been the most studied substance and a wide number of measurements of the enthalpy of sublimation by indirect methods have been carried out. All of them are consistent with each other and with the recommended value. Our result of $(96.31 \pm 0.72)\,\mathrm{kJ\,mol^{-1}}$ is slightly lower than those data. Though this can be explained by the fact that measurements for this compound were performed at a higher temperature (near 500 K) and some decomposition and loss of mass before vaporization is difficult to control. However, this result is closer to the recommended value than previous measurements performed by DSC [10] or thermogravimetry [27].

Table 6
Comparison with the literature values of the enthalpies of sublimation experimental and at $T = 298.15\,\text{K}$ of the studied aromatic hydrocarbons

Reference	Method	Temperature (K)	$\Delta_{\text{sub}}H(T)$ (kJ mol^{-1})	$\Delta_{\text{sub}}H(298.15)$ (kJ mol^{-1})
β-Naphthol				
[20]	Mass effusion	305–323	94.2 ± 0.5	94.7 ± 0.5
[21]	Mass effusion	277–324	87.4 ± 2.5	87.5 ± 2.5
[22]	Vapor pressure	283–323	78.7 ± 0.8	78.8 ± 0.8
[23]	Vapor pressure	568	68.3 ± 1.0[a]	78.3 ± 1.0[a]
This work	DSC	408.15	81.4 ± 1.2	85.5 ± 1.2
Phenanthrene				
[3]	Calorimetry	373	89.2 ± 0.3	90.9 ± 4.2
[14]	DSC	350	87.2 ± 1.1	90.9 ± 1.7
[24]	Gas saturation	313–453	88.9 ± 0.9	91.1 ± 0.9
[25]	Weighing effusion	315–335	90.5 ± 1.0	92.5 ± 2.0
[26]	Mass effusion	310–323	86.6 ± 0.8	87.1 ± 0.8
[16]	Recommended value			91.3 ± 2.7
This work	DSC	388.15	84.3 ± 0.8	89.6 ± 0.8
Pyrene				
[4]	Calorimetry	348–419	97.7 ± 0.5	101.0 ± 0.5
[4]	Mass effusion	348–419	97.5 ± 1.5	100.8 ± 1.5
[24]	Gas saturation	313–453	97.9 ± 1.0	94.4 ± 1.0
[26]	Mass effusion	342–358	94.5 ± 1.0	95.7 ± 1.0
[16]	Recommended value			100.2 ± 3.6
This work	DSC	443.15	80.9 ± 1.0	98.5 ± 1.0
Anthracene				
[10]	DSC	420–540	126.0 ± 4.0	129.5 ± 4.0
[24]	Gas saturation	313–453	99.7 ± 1.0	101.5 ± 1.0
[25]	Mass effusion	337–361	100.4 ± 1.0	104.5 ± 1.5
[26]	Mass effusion	339–354	102.1 ± 2.1	103.1 ± 2.1
[27]	Thermogravimetry	290–358	84.1 ± 3.1	84.8 ± 3.1
[16]	Recommended value			103.4 ± 2.7
This work	DSC	498.15	98.5 ± 1.0	96.3 ± 0.7

[a] The uncertainty assigned to this data of enthalpy of sublimation is an estimated value.

4. Conclusion

We conclude that measurements of the vaporization process at constant pressure and isothermally, as carried out in this work, produce results in very good agreement to results obtained by others calorimetric or indirect techniques, developed and performed by others recognized authors. Even in the case of anthracene and phenanthrene, the experimental device has the sensitivity and is able to distinguish the magnitude of enthalpy of sublimation for each isomer. This feature is fundamental for the application of this technique in thermochemical studies of other interesting organic compounds.

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References

[1] C. Hansen, C.A. Eckert, J. Chem. Eng. Data 31 (1986) 1.
[2] R. Bender, V. Bieling, G. Maurer, J. Chem. Thermodyn. 15 (1983) 585.

[3] E. Morawetz, J. Chem. Thermodyn. 4 (1972) 455.
[4] L. Malaspina, G. Bardi, R. Gigli, J. Chem. Thermodyn. 6 (1974) 1053.
[5] H.L. Finke, J.F. Messerly, S.H. Lee, A.G. Osborn, D.R. Dousslin, J. Chem. Thermodyn. 9 (1977) 937.
[6] C.G. De Kruif, R. Kuipers, J.C. Van Miltenburg, R.C.F. Schaake, G. Stevens, J. Chem. Thermodyn. 13 (1981) 1081.
[7] R. Sabbah, I. Antipine, M. Coten, L. Davy, Thermochim. Acta 115 (1987) 153.
[8] L. Malaspina, R. Gigli, G. Bardi, J. Chem. Phys. 59 (1973) 387.
[9] S. Murata, M. Sakiyama, S. Seki, J. Chem. Thermodyn. 14 (1982) 707.
[10] G. Beech, R.M. Lintonbon, Thermochim. Acta 2 (1971) 86.
[11] J.P. Murray, K.J. Cavell, J.O. Hill, Thermochim. Acta 36 (1980) 97.
[12] R.E. Farritor, L.C. Tao, Thermochim. Acta 1 (1970) 297.
[13] I. Mita, I. Imai, H. Kambe, Thermochim. Acta 2 (1971) 337.
[14] L.A. Torres-Gómez, G. Barreiro-Rodríguez, A. Galarza-Mondragón, Thermochim. Acta 124 (1988) 229.
[15] A. Rojas-Aguilar, E. Orozco-Guareño, M. Martinez-Herrera, J. Chem. Thermodyn. 33 (2001) 1405.
[16] R. Sabbah (Ed.), Reference Materials for Calorimetry and Differential Thermal Analysis, Thermochim. Acta 331 (1999) 93.
[17] T.B. Coplen, Atomic weights of the elements 1995, Pure Appl. Chem. 68 (1996) 2339.
[18] M. Frenkel, Thermodynamics of Organic Compounds in the Gas State, vols. I and II, College Station, TX, 1994.
[19] P.R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 1969.
[20] M. Colomina, M.V. Roux, C. Turrion, J. Chem. Thermodyn. 6 (1974) 571.
[21] M.R. Arshadi, J. Chem. Soc. Faraday Trans. I 70 (1974) 1569.
[22] N.V. Karyakin, I.B. Rabinovich, L.G. Pakhomov, Russ. J. Phys. Chem. 42 (1968) 954.
[23] O.E. May, J.F.T. Berliner, D.F.J. Lynch, J. Am. Chem. Soc. 48 (1926) 1274.
[24] K. Nass, D. Lenoir, A. Kettrup, Angew. Chem. Int. Ed. Engl. 34 (1995) 1735.
[25] C.G. De Kruif, J. Chem. Thermodyn. 12 (1980) 243.
[26] R.S. Bradley, T.G. Cleasby, J. Chem. Soc. Lond. (1953) 1690.
[27] H.G. Wiedeman, Thermochim. Acta 3 (1972) 355.