



Reconciled thermophysical data for anthracene

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ABSTRACT

Anthracene (CAS RN: 120-12-7) is recommended as a primary standard for sublimation enthalpy measurements and it is also frequently used for testing apparatus for vapour pressure measurements. Two recent recommendations by ICTAC for sublimation enthalpy at 298.15 K obtained by extrapolation can be found in the literature. However, no recommended vapour pressure equation and sublimation enthalpy as a function of temperature were reported. The following steps were performed to develop recommended sublimation pressure and enthalpy data for anthracene in the temperature range in which the calibrations are typically performed: (i) analysis and reconciliation of the literature values on vapour pressures and examination of their thermodynamic consistency with related thermal properties; (ii) new extensive vapour pressure measurements in the temperature range (343–373) K; (iii) calculation of ideal-gas thermodynamic properties combining statistical thermodynamics and quantum chemistry methods, and (iv) multi-property correlation of selected vapour pressure and thermal data. The quality and range of available data needed for the multi-property correlation allowed to establish the recommended sublimation pressure equation in the temperature range (200–373) K while at higher temperatures and for the liquid phase only tentative data are provided. Recommended values at 298.15 K are (0.91 ± 0.09) mPa for sublimation pressure and (101.01 ± 0.52) kJ·mol⁻¹ for sublimation enthalpy; the recommended enthalpy of sublimation at 0 K is (104.4 ± 0.9) kJ mol⁻¹. Based on the recommended sublimation pressures, super cooled liquid vapour pressures required for environmental modeling were also calculated.

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1. Introduction

Anthracene is recommended by ICTAC as a primary standard for the measurements of sublimation enthalpy and for testing of experimental setups for vapour pressure measurements for crystals exhibiting the vapour pressure from (0.1 to 1) Pa in the temperature range approximately (338–360) K [1]. Two most recent recommendations of sublimation enthalpy of anthracene at 298.15 K, $\Delta_{\text{cr}}^{\text{s}}H_{\text{m}}(298.15 \text{ K})$, are due to the ICTAC working group “thermochemistry” [1,2]. In 1999, Sabbah et al. [1] recommended $\Delta_{\text{cr}}^{\text{s}}H_{\text{m}}(298.15 \text{ K}) = (103\,360 \pm 2\,670)$ J·mol⁻¹ while in 2008 Roux et al. [2] included more recent data and suggested the recommended value $\Delta_{\text{cr}}^{\text{s}}H_{\text{m}}(298.15 \text{ K}) = (101.9 \pm 1.3)$ kJ·mol⁻¹. This rep-

resents relatively large change (and large uncertainty) for a standard denoted as primary. Although anthracene is proposed for testing the vapour pressure equipment for low volatile crystals, no recommended vapour pressure equation was established yet. Vapour pressure of anthracene has been measured by many researchers since the beginning of 20th century, but the mutual agreement between individual datasets is inconclusive. Despite this fact, anthracene was used for calibration or testing of new apparatus for vapour pressure measurements in many cases [3–18]. New measurements, which would resolve discrepancies in the literature data, seem therefore highly desirable. Thus this work was initiated with the aim of providing thermodynamically consistent reference data for both crystalline and liquid phases. We first assessed all the available literature vapour pressure data and examined their consistency with calorimetrically determined sublimation or vaporisation enthalpies and heat capacities of condensed phases and ideal gas. A literature review and consistency tests revealed inconsistencies in the data for the liquid phase indicating a need of new data and also a need for new vapour pressure data for crystalline phase in the low-pressure region for

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reconciliation of several available data sets of comparable uncertainty. The vapour pressure data in the low-pressure region were experimentally determined in this work. Also, thermodynamic properties in the ideal-gas state were calculated using the methods of statistical thermodynamics. Consequently, recommended vapour pressure data for crystalline anthracene in the temperature range (200–373) K were developed by the simultaneous correlation of selected vapour pressure and related thermal data (SimCor method, described previously [19] and for reader's convenience also in the Supplementary data). Tentative vapour pressure data are provided for crystalline anthracene in the temperature range (373–489) K and liquid anthracene in the temperature range (489–618) K. The sublimation enthalpy at 0 K was also evaluated in this work as it is used for benchmarking the lattice energy calculations [20–22].

2. Experimental

2.1. Materials

Commercially available anthracene was purchased from Aldrich. Mole fraction purity of anthracene sample was determined by gas-liquid chromatography to be $x = 0.9966$. Two impurities were found and identified by the gas-liquid chromatography with a mass-spectrometer detector (GLC-MS) as phenanthrene ($x = 0.0004$) and a compound with molecular formula $C_{12}H_8S$ ($x = 0.0030$). According to the available information [23], we deduced the unknown impurity to be naphtho[2,3-*b*]thiophene (the deduction is described in more detail in Section 2 in the Supplementary data). To prove the hypothesis, we synthesized naphtho[2,3-*b*]thiophene (for details, see Section 2.1 in the Supplementary data) and analysed it by GLC-MS. The retention time and mass spectrum perfectly matched with the impurity detected in anthracene sample. Samples characteristics are summarized in Table 1.

Table 1
Sample description.

Chemical Name	Source	Initial Mole Fraction Purity	Purification Method	Final Mole Fraction Purity	Analysis Method
Anthracene	Aldrich	0.995 ^a	none	0.9966	GLC ^b , GLC-MS ^c
naphtho[2,3- <i>b</i>]thiophene	synthesized ^d			0.9880	GLC-MS

^a Gas-liquid chromatography, value given in the Certificate of Analysis.

^b Gas-liquid chromatography analysis done in this work by Hewlett-Packard 6890 gas chromatograph equipped with a column HP-1, length 25 m, film thickness 0.52 μm , i.d. 0.32 mm, and FID detector.

^c Gas-liquid chromatography-mass spectrometry analysis done in this work by Agilent 7010 Triple Quadrupole GLC-MS System equipped with a column Rxi-5MS (Restek), length 20 m, film thickness 0.30 μm , i.d. 0.18 mm. Mass spectra database: NIST/EPA/NIH Mass Spectral Library (NIST 14).

^d See Section 2.1 in the Supplementary data for synthesis details.

Table 2
Experimental vapour pressures p for crystalline anthracene.^a

T/K	p^b/Pa	T/K	p^b/Pa	T/K	p^b/Pa	T/K	p^b/Pa
343.29	0.192	350.76	0.401	358.18	0.798	367.97	1.927
343.30	0.182	350.79	0.384	360.63	1.000	367.97	1.947
343.31	0.197	353.04	0.479	360.66	0.992	367.98	1.941
345.76	0.235	353.04	0.485	360.68	0.998	370.43	2.398
345.76	0.240	353.19	0.498	362.95	1.230	370.44	2.418
345.79	0.247	355.68	0.630	362.95	1.232	370.44	2.409
348.21	0.317	355.73	0.626	363.13	1.244	372.85	2.980
348.21	0.305	355.74	0.623	365.54	1.550	372.89	2.973
348.27	0.297	358.14	0.799	365.55	1.551	372.89	2.978
350.75	0.392	358.15	0.784	365.56	1.562		

^a The standard uncertainty in the sample temperature is $u(T) = 0.01$ K and the combined expanded uncertainty of vapour pressure measurements (0.95 level of confidence, $k = 2$) is $U_c(p/\text{Pa}) = 0.01 (p/\text{Pa}) + 0.05$ Pa.

^b Values are reported with one digit more than is justified by the experimental uncertainty to avoid round-off errors in calculations based on these results.

The anthracene sample was used as received as our estimation (see Section 2.2 in the Supplementary data) suggested that the two identified impurities in our anthracene sample cannot significantly influence measured sublimation pressures.

2.2. Vapour pressure measurements

The vapour pressure measurements were performed using the static method with an apparatus internally denoted as STAT 8 employing a capacitance diaphragm absolute gauge. As this apparatus was described in detail previously [24], only the principal characteristics are provided here. The operating pressure and temperature ranges are (0.1–1333) Pa and (273–373) K, respectively, and the standard uncertainty of the sample temperature and the resulting combined expanded uncertainty of vapour pressure measurements (0.95 level of confidence, $k = 2$) are $u(T) = 0.01$ K and $U_c(p/\text{Pa}) = 0.01 (p/\text{Pa}) + 0.05$, respectively.

3. Results and discussion

3.1. Vapour pressures

The vapour pressure measurement of anthracene was performed in the temperature interval (343–373) K by repeatedly varying the selected temperatures in a random order to detect systematic errors caused by insufficient degassing of the sample. A full automation of the STAT8 apparatus allowed us to perform a high number of measuring cycles, which led to lowering of the observed pressure with the number of measuring cycles. After completing hundreds of measuring cycles at selected temperatures, the pressure decrease was negligible and the final set of data was recorded. Final set of experimental vapour pressures obtained in this work is given in Table 2.

The number of data sets on vapour pressure of crystalline anthracene reported in the literature is large. For brevity, only data

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