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Fluorene: An extended experimental thermodynamic study

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ABSTRACT

This work reports new experimental thermodynamic results on fluorene. Vapor pressures of both crystalline and liquid phases were measured using a pressure gauge (capacitance diaphragm manometer) and Knudsen effusion methods over a wide temperature range (292.20 to 412.16) K yielding accurate determination of enthalpy and entropy of sublimation and of vaporization. The enthalpy of sublimation was also determined using Calvet microcalorimetry. The enthalpy of fusion was derived from vapor pressure results and from d.s.c. experiments. Static bomb calorimetry was used to determine the enthalpy of combustion of fluorene from which the standard enthalpy of formation in the crystalline phase was calculated. The enthalpy of formation in the gaseous phase was calculated combining the result derived for the crystalline phase with the enthalpy of sublimation.

1. Introduction

Nowadays, the availability of reliable information on physical–chemical properties of fluorene and of compounds with a fluorene core is very important. Several of these polycyclic aromatic hydrocarbons (PAHs) present good performance as active components in a new generation of electronic devices, mainly as organic light-emitting diodes (OLEDs). Typically, they have low vapor pressures and consequently they are persistent in the environment with tendency to accumulate in living beings, soils, and sediments and are also highly dispersed by the atmosphere [1]. As their industrial use keeps growing, control of their emissions is an important issue considering the adverse health effects associated with exposure to these substances. The prediction of the behavior and reaction kinetics of these substances requires an accurate description of their thermochemical and thermophysical properties which are also very useful in designing processes to generate new ones and for predicting their potential for application in electronic devices. However, available experimental thermochemical and thermophysical data on these compounds are scarce and when available is often inaccurate [1]. For fluorene ($C_{13}H_{10}$), the enthalpy of formation in the condensed state and the enthalpy of sublimation have been reported in the literature several times. In a recent review by Roux *et al.* [1], a very useful summary of relevant thermochemical and thermophysical properties of several PAHs is presented. Recommended for fluorene are the values $(90.2 \pm 2.8)\ \mathrm{kJ \cdot mol^{-1}}$ and $(86.5 \pm 1.3)\ \mathrm{kJ \cdot mol^{-1}}$, respectively, for its enthalpy of formation, in crystalline phase, and for its enthalpy of sublimation yielding the value $(176.7 \pm 3.1)\ \mathrm{kJ \cdot mol^{-1}}$ for its enthalpy of formation in the gaseous phase. Recently, however, this property was derived as $191.9\ \mathrm{kJ \cdot mol^{-1}}$ [2] ($15.2\ \mathrm{kJ \cdot mol^{-1}}$ higher than the recommended value) from DFT calculations. Since accurate results of vapor pressure and enthalpies of formation of fluorene are of crucial importance for rationalizing the results derived for some fluorene derivatives, presently under study in our research group, we decided to perform an extended experimental thermodynamic study of this compound. So, this paper reports thermodynamic results for fluorene derived by static bomb calorimetry, vapor pressure measurements (using two different methods), Calvet microcalorimetry and d.s.c.

2. Experimental

2.1. Purification and purity control

Fluorene [CAS registry no. 86-73-7] was purchased from Aldrich Chemical Co. with the specification of an average mole fraction purity of 0.9980. The measurement of the mole fraction for the original sample, by gas chromatography (using an apparatus Agilent, model 4890D, equipped with a flame ionization detector detector) led to the value 0.9898. The commercial product was sublimed

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under reduced pressure, at *ca.* $T = 373$ K, but the GC analysis of the sublimed sample evidenced the existence of the impurity detected previously, which had a retention coefficient very similar to that of fluorene. This sample was then re-crystallized several times from tetrahydrofurane, and dried under reduced pressure, until the GC analysis confirmed a minimum mole fraction purity of 0.9991. The purity of the sample was also confirmed by the ratio of the mass of carbon dioxide recovered in the combustion experiments to that calculated from the mass of the sample; the average ratio and the respective uncertainty (twice the standard deviation of the mean), was (1.0005 ± 0.0005). The specific density of the sample is $\rho = 1.20\ \mathrm{g \cdot cm^{-3}}$[3].

2.2. Static bomb combustion calorimetry

The energy of combustion of fluorene was measured by static bomb calorimetry, using a calorimeter provided with a bomb equipped with a twin valve system and presenting an internal volume 0.290 $\mathrm{dm^3}$ [4–6]. The energy equivalent of the calorimeter ε(calor) was determined using benzoic acid [CAS 65-85-0], Standard Reference Material (SRM 39j) supplied by the National Institute of Standards and Technology (NIST), having a massic energy of combustion, under bomb conditions, of $-(26434 \pm 3)\ \mathrm{J \cdot g^{-1}}$. The energy equivalent of the calorimeter $\varepsilon(\text{calor}) = (15551.7 \pm 1.2)\ \mathrm{J \cdot K^{-1}}$ (the uncertainty quoted is the standard deviation of the mean), corresponding to an average mass of 2900.0 g of water used as calorimetric fluid, was determined from eight calibration experiments, made under oxygen at $p = 3.04$ MPa and using 1.00 $\mathrm{cm^3}$ of water added to the bomb. All the samples were ignited at $T = (298.150 \pm 0.001)$ K, in oxygen at $p = 3.04$ MPa, with 1.00 $\mathrm{cm^3}$ of deionised water previously added to the bomb. The electrical energy for ignition ΔU(ign.) was determined from the change in potential difference across a 1400 μF capacitor when discharged through the platinum ignition wire. For the cotton thread fuse, of empirical formula $\mathrm{CH_{1.686}O_{0.843}}$, the massic energy of combustion is $\Delta_c u^o = -16{,}240\ \mathrm{J \cdot g^{-1}}$ [7]. The corrections for nitric acid formation, $\Delta U(\mathrm{HNO_3})$, were based on the value $-59.7\ \mathrm{kJ \cdot mol^{-1}}$ [8], for the molar energy of formation of $0.1\ \mathrm{mol \cdot dm^{-3}}$ $\mathrm{HNO_3(aq)}$ from $\mathrm{N_2(g)}$, $\mathrm{O_2(g)}$, and $\mathrm{H_2O(l)}$. An estimated pressure coefficient of specific energy: $(\partial u/\partial p)_T = -0.2\ \mathrm{J \cdot g^{-1} \cdot MPa^{-1}}$ at $T = 298.15$ K, a typical value for most organic compounds [9], was assumed. The mass of compound, m(cpd), used in each experiment was determined from the total mass of carbon dioxide, $m(\mathrm{CO_2}$, total), produced after allowance for that formed from the combustion of the cotton thread. For each compound, the standard massic energy of combustion, $\Delta_c u^o$, was calculated by the procedure given by Hubbard *et al.* [10].

2.3. Phase transitions

2.3.1. d.s.c. Measurements

A power compensated differential scanning calorimeter (Setaram 141) was used to determine the temperatures and enthalpies of fusion of fluorene. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction purity > 0.99999). The temperature scale of the calorimeter was calibrated by measuring the melting temperature of the following high purity reference materials [11]: naphthalene, benzoic acid, and indium. Six independent scans were performed under nitrogen atmosphere using a heating rate of $3.3 \cdot 10^{-2}\ \mathrm{K \cdot s^{-1}}$. No crystalline transitions were detected above the temperature 298 K.

2.3.2. Vapor pressures and enthalpies of sublimation and of vaporization

The vapor pressure of fluorene was measured at different temperatures in both crystalline and liquid phases enabling the indirect determination of enthalpies and entropies of sublimation and of vaporization. The vapor pressure of the crystalline phase was measured from $T = (292.20$ to $320.10)$ K using the Knudsen mass-loss effusion method and from $T = (312.89$ to $378.50)$ K using a pressure gauge static method. The latter method was also used to measure the vapor pressures of the liquid from $T = (386.48$ to $412.16)$ K.

The Knudsen effusion apparatus used was previously described in detail [12]. This apparatus enables the simultaneous operation of nine effusion cells, contained in cylindrical holes inside three temperature-controlled aluminum blocks. During an effusion experiment, each aluminum block, containing three effusion cells, is kept at a constant temperature, different from the other two blocks. Three different groups of effusion cells, according to the different areas of the effusion orifices, were used: one "*small*" ($A_o \approx 0.5\ \mathrm{mm^2}$: series A), one "*medium*" ($A_o \approx 0.8\ \mathrm{mm^2}$: series B) and one "*large*" ($A_o \approx 1.1\ \mathrm{mm^2}$: series C). The temperature of each block is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four wire connection) previously calibrated by comparison with an SPRT (25 Ω; Tinsley, 5187 A). The exact areas and Clausing factors of each effusion orifice used, made in platinum foil of 0.0125 mm thickness, are presented in the supporting information, table S1. In each effusion experiment, the mass loss of the crystalline sample, Δm, was measured by weighing the cells, within ±0.01 mg, before and after a convenient effusion time period, t, in a system evacuated to a pressure near $1 \cdot 10^{-4}$ Pa. For the temperature T, the vapor pressure p of the sample contained in each effusion cell is calculated by equation (1) where M is the molar mass of the effusing vapor, R is the gas constant, A_o represents the area of the effusion orifice and w_o is the respective Clausing factor. The uncertainty of the measured temperatures is estimated to be ±0.01 K and that of the measured pressures is estimated to be better than ±0.01 Pa.

$$p = (m/A_o w_o t) \cdot (2\pi RT/M)^{1/2}. \tag{1}$$

The static apparatus used is based on capacitance diaphragm gauges and was also previously described in detail [13]. The two capacitance diaphragm absolute gauges available in this apparatus were obtained from MKS Instruments, Inc. They operate at self-controlled constant temperatures: gauge 1, Baratron 631A01TBEH ($T_{\text{gauge}} = 423$ K) for measuring pressures over the range (0.4 to 133) Pa and temperature from (253 to 413) K; gauge 2, Baratron 631A11TBFP ($T_{\text{gauge}} = 473$ K) capable of measuring pressures over the range (3 to 1330) Pa and temperature from (253 to 463) K. A platinum resistance thermometer Pt100 class 1/10 (in a four wire connection) was used to measure the temperature of the condensed samples. This thermometer was calibrated by comparison with a SPRT (25 Ω; Tinsley, 5187 A). The metal tubing between the cell containing the condensed sample and the pressure gauge is kept at a temperature higher than the temperature of the sample and lower than the temperature of the gauge. The uncertainty of the temperature measurements is estimated to be better than ±0.01 K and the uncertainty in the pressure measurements is adequately described by the expressions $\sigma(p/\mathrm{Pa}) = 0.01 + 0.0025\ (p/\mathrm{Pa})$ for gauge 1 and $\sigma(p/\mathrm{Pa}) = 0.1 + 0.0025\ (p/\mathrm{Pa})$ for gauge 2.

The enthalpy of sublimation of fluorene was also determined calorimetrically using a Calvet High Temperature Microcalorimeter (Setaram, HT 1000D) for applying the "vacuum sublimation drop-microcalorimetric technique" proposed by Skinner *et al.* [14]. The apparatus and technique have been previously described [15]. The microcalorimeter was calibrated *in situ* for these measurements using the reported standard molar enthalpy of sublimation of naphthalene (Aldrich, mole fraction purity > 0.99), $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(T = 298.15\ \mathrm{K}) = (76.60 \pm 0.60)\ \mathrm{kJ \cdot mol^{-1}}$ [11,16]. The calibration constant, k, of the calorimeter, at the experimental temperature used to sublime fluorene, was found to be $k(T = 368.8\ \mathrm{K}) = (0.9916 \pm$