



Solid vapor pressure for five heavy PAHs via the Knudsen effusion method

Jinxia Fu^{a,*}, Eric M. Suuberg^b

^a Brown University Department of Chemistry, Providence, RI 02912, USA

^b Brown University School of Engineering, Providence, RI 02912, USA

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are compounds resulting from incomplete combustion and many fuel processing operations, and they are commonly found as subsurface environmental contaminants at sites of former manufactured gas plants. Knowledge of their vapor pressures is the key to predict their fate and transport in the environment. The present study involves five heavy PAHs, *i.e.* benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, and dibenz[*a,h*]anthracene, which are all as priority pollutants classified by the US EPA. The vapor pressures of these heavy PAHs were measured by using Knudsen effusion method over the temperature range of (364 to 454) K. The corresponding values of the enthalpy of sublimation were calculated from the Clausius–Clapeyron equation. The enthalpy of fusion for the five PAHs was also measured by using differential scanning calorimetry and used to convert earlier published sub-cooled liquid vapor pressure data to solid vapor pressure in order to compare with the present results. These adjusted values do not agree with the present measured actual solid vapor pressure values for these PAHs, but there is good agreement between present results and other earlier published sublimation data.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the main classes of persistent organic pollutants which occur naturally in petroleum and result from incomplete combustion and many fuel processing operations. Sixteen PAHs are listed as priority pollutants by the US Environmental Protection Agency (US EPA). Health effects are of concern due to their persistence, toxic and carcinogenic properties. The thermodynamic properties of PAHs have been widely studied for more than 50 years [1–22].

Vapor pressure is a fundamental property which is the key to predict the fate and transport of a substance in the environment. Many experimental techniques have been developed to measure the vapor pressure of PAHs, such as the Knudsen effusion method [9–11,17,21], the generator column–HPLC method [5], the gas saturation method [19], the electronic manometry method [23], and the GC-retention time method [14,20]. Several compendia of vapor pressures for PAHs have also been published, which detail many correlations and also uncertainties in current experimental data [1–4]. However, many of the previous studies have focused on light PAHs, and only limited vapor pressure data exist for heavy PAHs. This is especially true for benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene, and

dibenz[*a,h*]anthracene, of which all are US EPA priority pollutants. The heavier PAHs are more persistent than the lighter PAHs and tend to have greater carcinogenic and other chronic impact potential.

In this study, the Knudsen effusion technique was used to measure the solid vapor pressures, their temperature dependence, and enthalpies of sublimation for five heavy PAHs, *i.e.* benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene and dibenz[*a,h*]anthracene. Additionally, the enthalpies of fusion, phase change of these PAHs, have also been studied by using differential scanning calorimetry.

2. Materials and methods

2.1. Materials

The five heavy polycyclic aromatic hydrocarbons that were examined fall in the molar mass (*M*) range from (252 to 278) g · mol^{−1}. They were purchased from TCI and Aldrich with minimum mass fraction purity 0.95, as detailed in table 1. They were used in the measurements without further purification.

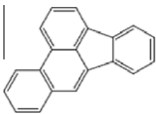
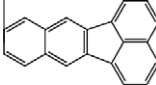
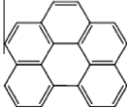
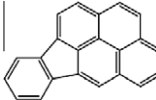
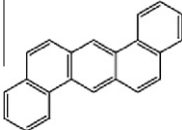
2.2. Enthalpies of fusion

The enthalpies of fusion were measured using a TA instruments 2910 differential scanning calorimeter (DSC). A 1 to 3 mg sample was placed into a hermetically sealed DSC pan and this was

* Corresponding author. Tel.: +1 401 863 2775; fax: +1 401 863 9120.

E-mail addresses: jinxia_fu@Brown.edu (J. Fu), Eric_Suuberg@Brown.edu (E.M. Suuberg).

TABLE 1
Polycyclic aromatic hydrocarbons examined.

CAS reg. no.	Compound	Min. purity	$M/(g \cdot mol^{-1})$	T_{fus}/K [3]	Molecular structure
205-99-2	Benzo[<i>b</i>]fluoranthene	0.95	252.31	441.15	
207-08-9	Benzo[<i>k</i>]fluoranthene	0.98	252.31	490.15	
191-24-2	Benzo[<i>ghi</i>]perylene	0.97	276.33	545.65	
193-39-5	Indeno[1,2,3- <i>cd</i>]pyrene	0.99+	276.33	435.15	
53-70-3	Dibenz[<i>a,h</i>]anthracene	0.95	278.35	542.65	

scanned in heating mode at a heating rate of $10 K \cdot min^{-1}$. The uncertainty in the DSC measurement is about $\pm 5 J \cdot g^{-1}$. The calibration of DSC consists of two procedures, baseline calibration and temperature calibration. The baseline calibration minimizes the temperature fluctuation in the heating process to permit the correct conversion of temperature difference to heat flow. This procedure is done by removing the pans from the DSC cell with the purge gas flow set at desired flow rate, $50 cm^3 \cdot min^{-1}$. The baseline obtained is used to calculate the slope and offset values. The temperature calibration uses standard indium which allows establishing both an accurate melting temperature and enthalpy. More details of this technique can be found in a previous publication [24].

2.3. Vapor pressure

The Knudsen effusion technique derives from Knudsen's 1909 Kinetic Theory of Gases. The Knudsen effusion method is an indirect measurement technique based on the molecular effusion of a vapor through an orifice into a high vacuum chamber and is generally used to measure the vapor pressure of low volatility substances. The present implementation of the Knudsen effusion method is described in a previous publication [24]. Samples were placed inside effusion cells prepared from steel shim stock. The cells were sealed except for a single, circular orifice (0.61 ± 0.02) mm in diameter, and then placed on one arm of a continuously recording microbalance in a high vacuum chamber. The pressure inside of the chamber was reduced to 10^{-4} Pa in the experiments. The measurements were made under isothermal conditions by using a type K thermocouple located above the effusion cell. More details of this technique may be found in Goldfarb and Suuberg [9] and Oja and Suuberg [17].

3. Results and discussion

DSC was used to study the enthalpies of fusion of these five PAHs and the data are compared with literature values in table 2. The value for benzo[*b*]fluoranthene is within the literature range, while the values for benzo[*k*]fluoranthene, benzo[*ghi*]perylene and dibenz[*a,h*]anthracene are about $0.2 kJ \cdot mol^{-1}$ to $2.3 kJ \cdot mol^{-1}$

TABLE 2
Enthalpy of fusion. Overview of the experimental data range ($\Delta_{fus}H(lit.)$) [1,25] and the DSC study here ($\Delta_{fus}H(DSC)$) for the five PAHs.

Compound	$\Delta_{fus}H(lit.)/(kJ \cdot mol^{-1})$	$\Delta_{fus}H(DSC)/(kJ \cdot mol^{-1})$
Benzo[<i>b</i>]fluoranthene	18.3 to 20.9	18.3
Benzo[<i>k</i>]fluoranthene	27.4 to 34.2	26.5
Benzo[<i>ghi</i>]perylene	16.5 to 18.3	16.3
Indeno[1,2,3- <i>cd</i>]pyrene	17.8 to 21.5	22.9
Dibenz[<i>a,h</i>]anthracene	26.8 to 31.2	24.5

lower than the published range of literature values. The enthalpy of fusion for indeno[1,2,3-*cd*]pyrene in this study is about $1.4 kJ \cdot mol^{-1}$ higher than literature values. Bearing in mind the measurement uncertainty of $\pm 5 J \cdot g^{-1}$, the present measured values would have an inherent uncertainty of $(1.3$ to $1.4) kJ \cdot mol^{-1}$.

The enthalpies of fusion data were used to correct the sub-cooled state vapor pressures to real solid vapor pressures (see below).

Table 3 presents the raw data obtained in the present experiment using the Knudsen effusion method. The reference compound anthracene was employed to test periodically the performance of the Knudsen effusion apparatus and the results are in good agreement with literature values [5,7,9,12] (see figure 1(a)). These data were used to calculate the enthalpy ($\Delta_{sub}H$) and entropy ($\Delta_{sub}S$) of sublimation, and vapor pressure at $T = 298.15 K$ using the Clausius–Clapeyron equation, integrated assuming a constant enthalpy of sublimation,

$$\ln \frac{P}{P_0} = -\frac{\Delta_{sub}H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right), \quad (1)$$

where R is the universal gas constant, T is the absolute temperature of the sample ($T < T_{fus}$), and P_0 and T_0 are values at a related reference condition.

Table 4 presents the results of fitting the data with the Clausius–Clapeyron equation (equation (1)) along with the statistical significance of these results. The enthalpy of sublimation value presented here is calculated from the slope of the Clausius–Clapeyron equation for the temperature range indicated in table 3. The vapor pressure at $T = 298.15 K$ was also calculated by using

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