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Thermochimica Acta 245 (1994) 121–144

thermochimica
acta

Vapor pressures for a group of high-boiling alkylbenzenes under environmental conditions ☆

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Abstract

Vapor pressures of high boiling pollutants are extremely low under ambient conditions; these data are, however, required with reasonable accuracy for better understanding and predicting the transport and fate of pollutants in the environment. Direct measurements of vapor pressures below 1 kPa are complicated and subject to systematic errors; it is therefore more suitable for combine experimental data at higher pressures with the related thermal data (heats of phase transition, heat capacities) available in the low pressure range. Such an extrapolation of vapor pressures controlled by exact thermodynamic relationships yields consistent data describing the vapor–liquid or vapor–solid saturation line under environmental conditions. The method has been used to generate recommended vapor pressures between 223.15 and 323.15 K for 20 alkylbenzenes with normal boiling temperatures above 423 K. All available primary literature data characterizing the vapor–liquid saturation line have been evaluated and the selected values are correlated using the three parameter Cox equation. For those compounds that are solid at ambient temperatures the thermodynamic calculation of vapor pressures below the triple point temperature is also performed. The recommended data are tabulated at discrete temperatures and presented also as parameters of correlating equations.

Keywords: Alkylbenzene; Database; Heat capacity; Heat of vaporization; High boiling; SSE; Vapour pressure; VLE; VSE

☆ Presented at the Czechoslovak–Franch–Polish Conference on Calorimetry and Experimental Thermodynamics: Applications to Contemporary Problems, Prague, Czech Republic, 4–7 September 1993.

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SSDI 0040-6031(94)01847-A

1. Introduction

An important number of high boiling organic compounds are classified as pollutants. Their vapor pressures are extremely low at ambient temperatures but are nevertheless required with reasonable accuracy for the evaluation of transport and fate of pollutants in the environment. Data available in different environmental databases were in some cases picked up more or less randomly from the literature; the values are often unverified and in many cases obviously doubtful. One source of vapor pressure data is direct low pressure experiments using saturation, effusion, and chromatographic methods; the values resulting from these techniques are, however, often subject to significant systematic errors. The second source is long extrapolations from the data available near the normal boiling temperature. In most cases these calculations were performed using simple relationships (such as the Antoine equation) which are not, however, able to describe satisfactorily the saturation line in a wide temperature range.

An alternative way for determining vapor pressure of high boiling compounds near room temperature is a combination of medium vapor pressure data (available generally between 1 and 100 kPa) with the related thermal data such as enthalpies of vaporization and the difference between heat capacity of an ideal gas and that of the liquid (denoted subsequently simply as the heat capacity difference). Unlike vapor pressures, thermal properties are known for a considerable number of organic compounds with reasonable accuracy at pressures well below the normal boiling temperature. Enthalpies of vaporization have been reported for several hundreds of organic compounds at or near 298.15 K which is well below T_b for many organic compounds. Heat capacities of an ideal gas, calculated from spectral data, are available for a large number of compounds at temperatures below T_b and heat capacities of liquids are accessible from calorimetric measurements down to the triple point.

The simultaneous correlation of vapor pressure and thermal data was first used by King and Al-Najjar [1] to obtain reliable values in the low pressure range for n-alkanes C_6 to C_{16} and later by other authors for different types of compounds [2–4]. This approach was also used to produce the recommended data on vapor pressures and enthalpies of vaporization down to the triple point temperature for C_5 to C_{20} n-alkanes [5] and for C_1 to C_{18} 1-alkanols [6]. Suitability of different correlating equations for the simultaneous correlation and efficiency of this method were recently evaluated by Růžička and Majer [7].

This work is concerned with the generation of recommended vapor pressures and enthalpies of vaporization for a group of 20 alkylbenzenes which are all listed in the environmental literature as pollutants: eight polymethylbenzenes, four alkylmethylbenzenes and eight monoalkylbenzenes. We include in our selection only those alkylbenzenes that have the normal boiling temperature above 423 K. Methylbenzene (toluene), dimethylbenzenes (xylenes) and ethylbenzene exhibit vapor pressures above 1 kPa at ambient temperature and are therefore available from direct experimental measurements with good accuracy. Isopropyl-4-methyl benzene (p-cymene) is included as a common chemical with a significant polluting character.

2. Thermodynamic background

2.1. Vapor–liquid saturation line

Vapor pressure p_{sat}, enthalpy of vaporization ΔH_{vap} and the heat capacity difference $\Delta C^{\ominus}_{\mathrm{vap}}$ are linked by the exact thermodynamic relationships. The latter quantity is defined as the difference between the heat capacity of an ideal gas and that of the liquid

$$\Delta C^{\ominus}_{\mathrm{vap}} = C^{\ominus}_p - C^{\mathrm{l}}_p \tag{1}$$

Simultaneous correlation of experimental data for the above three quantities as a function of temperature allows a consistent description of the vapor–liquid saturation line. Such an approach can be applied easily below atmospheric pressure where deviations of vapor volume from nonideality are low and can be estimated or, at sufficiently low pressures, neglected. This is particularly advantageous for determining the vapor pressure down to the triple point temperature. Combination of this value with the thermal data describing the sublimation equilibria allows the vapor pressures characterizing the vapor–solid saturation line to be calculated. Basic relationships are reviewed below; for a more detailed description the reader should refer to the monograph by Majer et al. [8].

Vapor pressure p_{sat} and enthalpy of vaporization ΔH_{vap} are related by the Clapeyron equation

$$RT^2\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_{\mathrm{sat}} = \frac{\Delta H_{\mathrm{vap}}}{\Delta Z_{\mathrm{vap}}} \tag{2}$$

where subscript "sat" denotes a derivative along the saturation line and $\Delta Z_{\mathrm{vap}} = Z^{\mathrm{g}}_{\mathrm{sat}} - Z^{\mathrm{l}}_{\mathrm{sat}}$ stands for the difference between the compressibility factors of the saturated vapor and that of the saturated liquid. The symbol $\Delta H'$ will be used below to denote the ratio of enthalpy of vaporization and the difference in the compressibility factors

$$\Delta H' = \frac{\Delta H_{\mathrm{vap}}}{\Delta Z_{\mathrm{vap}}} \tag{3}$$

For convenience let us define a new quantity $\Delta C'$ as a temperature derivative of $\Delta H'$ along the saturation line

$$\Delta C' = \left(\frac{\mathrm{d}\Delta H'}{\mathrm{d}T}\right)_{\mathrm{sat}} \tag{4}$$

By combining Eqs. (3) and (4) one obtains

$$\Delta C' = \left(\frac{\mathrm{d}\Delta H_{\mathrm{vap}}}{\mathrm{d}T}\right)_{\mathrm{sat}} \frac{1}{\Delta Z_{\mathrm{vap}}} - \left(\frac{\mathrm{d}\Delta Z_{\mathrm{vap}}}{\mathrm{d}T}\right)_{\mathrm{sat}} \frac{\Delta H_{\mathrm{vap}}}{\Delta Z^2_{\mathrm{vap}}} \tag{5}$$

The volumetric properties of the vapor phase at conditions below the normal boiling temperature can be most suitably described by the virial expansion explicit in volume, limited to the second virial coefficient B which is a function of temperature

$$V^{\mathrm{g}} = \frac{RT}{p_{\mathrm{sat}}} + B \tag{6}$$

The difference in the compressibility factors of the saturated phases can be then written as

$$\Delta Z_{\mathrm{vap}} = 1 + \frac{p_{\mathrm{sat}}}{RT}(B - V^{\mathrm{l}}) \tag{7}$$

where V^{l} is the molar volume of the liquid. By combining Eqs. (3) and (7) one obtains

$$\Delta H' = \frac{\Delta H_{\mathrm{vap}}}{1 + \frac{p_{\mathrm{sat}}}{RT}(B - V^{\mathrm{l}})} \tag{8}$$

and similarly combination of Eqs. (2), (5) and (7) results in the relationship between $\Delta C'$ and the heat capacity difference $\Delta C^{\ominus}_{\mathrm{vap}}$

$$\Delta C' = \Delta C^{\ominus}_{\mathrm{vap}} - Tp_{\mathrm{sat}}\frac{\mathrm{d}^2 B}{\mathrm{d}T^2} - 2T\frac{\mathrm{d}(B - V^{\mathrm{l}})}{\mathrm{d}T}\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\mathrm{sat}} - T(B - V^{\mathrm{l}})\left(\frac{\mathrm{d}^2 p}{\mathrm{d}T^2}\right)_{\mathrm{sat}} \tag{9}$$

Eqs. (8) and (9) enable the quantities $\Delta H'$ and $\Delta C'$ to be expressed from the experimental thermal data. Importance of the pVT terms will decrease with the decreasing vapor pressure and at a sufficiently low pressure $\Delta H' = \Delta H_{\mathrm{vap}}$ and $\Delta C' = \Delta C^{\ominus}_{\mathrm{vap}}$ within the limits of experimental error.

By combining Eqs. (2) and (3) we obtain

$$\Delta H' = RT^2\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_{\mathrm{sat}} = -R\left(\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)}\right)_{\mathrm{sat}} \tag{10}$$

and by introducing this relationship into Eq. (4) it follows that

$$\Delta C' = R\left[\frac{\mathrm{d}}{\mathrm{d}T}T^2\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)\right]_{\mathrm{sat}} = 2RT\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_{\mathrm{sat}} + RT^2\left(\frac{\mathrm{d}^2\ln p}{\mathrm{d}T^2}\right)_{\mathrm{sat}} \tag{11}$$

The last two relationships allow the expression of $\Delta H'$ and $\Delta C'$ exclusively from a vapor pressure equation. The possibility of expressing $\Delta H'$ and $\Delta C'$ both from the thermal and vapor pressure data means that after selecting a suitable relationship describing p_{sat} versus T it is possible to correlate simultaneously experimental p_{sat}, ΔH_{vap} and $\Delta C^{\ominus}_{\mathrm{vap}}$ as a function of temperature. The parameters of a vapor pressure equation are then obtained by minimizing an objective function S which can be defined as

$$S = \sum_{i=1}^{t}\frac{(\ln p^{\mathrm{exp}}_{\mathrm{sat}} - \ln p^{\mathrm{sm}}_{\mathrm{sat}})^2_i}{\sigma^2_i \ln p_{\mathrm{sat}}} + K^2_H\sum_{j=1}^{u}\frac{(\Delta H'^{\mathrm{exp}} - \Delta H'^{\mathrm{sm}})^2_j}{\sigma^2_j\,\Delta H'} + K^2_C\sum_{k=1}^{v}\frac{(\Delta C'^{\mathrm{exp}} - \Delta C'^{\mathrm{sm}})^2_k}{\sigma^2_k\,\Delta C'} \tag{12}$$

The quantities with the superscript "exp" relate to the experimental data ($\Delta H'^{\mathrm{exp}}$ and $\Delta C'^{\mathrm{exp}}$ are calculated from thermal data using Eqs. (8) and (9)); the quantities with the superscript "sm" are expressed from a vapor pressure equation ($\Delta H'^{\mathrm{sm}}$ and $\Delta C'^{\mathrm{sm}}$ are calculated from Eqs. (10) and (11)). Indices t, u, v indicate respectively the total number of experimental p_{sat}, ΔH_{vap} and $\Delta C^{\ominus}_{\mathrm{vap}}$ values included in the correlation. K_H, K_C are the weighting factors of the thermal properties which allow the impact of the thermal data on the final fit to be increased or decreased. The weighting factors can differ from unity especially when the numbers of data points for the three correlated quantities differ significantly or when an obvious inconsistency is observed. The variances $\sigma^2 \ln p_{\mathrm{sat}}$, $\sigma^2 \Delta H'$ and $\sigma^2 \Delta C'$ were estimated from the expected errors of experimental data points. The quantity $\sigma^2 \ln p_{\mathrm{sat}}$ was obtained as a statistical estimate from the expected errors in temperature σT and pressure σp

$$\sigma^2 \ln p_{\mathrm{sat}} = \left(\frac{\sigma p}{p}\right)^2 + \left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)^2_{\mathrm{sat}} (\sigma T)^2 \tag{13}$$

Similarly $\sigma^2 \Delta C'$ was estimated from the expected errors in $C_p^{\ominus}$ and C_p^{l} as

$$\sigma^2 \Delta C' = (\sigma C_p^{\ominus})^2 + (\sigma C_p^{\mathrm{l}})^2 \tag{14}$$

$\sigma^2 \Delta H'$ was obtained from the error in the enthalpy of vaporization as $\sigma^2 \Delta H' = (\sigma\ \Delta H_{\mathrm{vap}})^2$. The effect of uncertainty in the volumetric correction terms (Eqs. (8) and (9)) was neglected as the thermal data were included only in the temperature intervals where the magnitude of the corrections was of the same order as that of expected error in the thermal data.

Selection of a flexible relationship, enabling several thermodynamic properties to be described simultaneously as a function of temperature, is crucial for the success of this type of correlation. The performance of different vapor pressure equations has been tested and discussed previously [7]. Finally, we have opted for the three parameter Cox equation

$$\ln\left(\frac{p_{\mathrm{sat}}}{p_0}\right) = \left(1 - \frac{T_0}{T}\right) \exp(A_0 + A_1 T + A_2 T^2) \tag{15}$$

using the normal boiling point as reference state ($p_0 = 101.325$ kPa, $T_0 = T_{\mathrm{b}}$). This equation gives a satisfactory fit with the lowest number of parameters and unlike the popular Wagner equation does not require the critical properties that are unavailable for high boiling compounds. In addition, in an earlier study [9] the Cox equation was found to be particularly well suited for extrapolations of vapor pressures from the medium pressure range down towards the triple point even without support of the thermal data.

Introduction of the Cox equation into the relationships (10) and (11) leads to the following expressions for $\Delta H'$ and $\Delta C'$:

$$\Delta H' = R \exp(A_0 + A_1 T + A_2 T^2)[T_0 + T(T - T_0)(A_1 + 2A_2 T)] \tag{16}$$

and

$$\Delta C' = RT \exp(A_0 + A_1 T + A_2 T^2)[2A_1 + 4A_2 T + (T - T_0)(2A_2 + A_1^2 + 4A_1 A_2 T + 4A_2^2 T^2)] \tag{17}$$

which are parameters relating the vapor pressure equation to the thermal data.

2.2. Vapor–solid saturation line

Vapor pressures characterizing the vapor–solid saturation line are usually low; in most cases the vapor phase obeys the ideal gas law and the Clapeyron Eq. (2) can be simplified to

$$RT^2\left(\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right)_{\mathrm{sat}} = \Delta H_{\mathrm{sub}} \tag{18}$$

The enthalpy of sublimation ΔH_{sub} as a function of temperature can be expressed from the relationship

$$\Delta H_{\mathrm{sub}} = (\Delta H_{\mathrm{mel}} + \Delta H_{\mathrm{vap}})_{\mathrm{t}} + \int_{T_{\mathrm{t}}}^{T} \Delta C_{\mathrm{sub}}^{\ominus}\,\mathrm{d}T \tag{19}$$

where both the enthalpy of vaporization ΔH_{vap} and the enthalpy of melting ΔH_{mel} relate to the triple point temperature T_{t}. Within experimental error of determination this temperature equals the melting point temperature (relating to the atmospheric pressure and presumably an air saturated sample). When the integration interval in Eq. (19) is not too large ($T - T_{\mathrm{t}} < 100$ K) the difference between the heat capacity of an ideal gas and that of the solid phase $\Delta C_{\mathrm{sub}}^{\ominus}$ can be approximated by a first degree polynomial in temperature

$$\Delta C_{\mathrm{sub}}^{\ominus} = C_p^{\ominus} - C_p^{\mathrm{s}} = E_1 + 2E_2T \tag{20}$$

In this case the combination of the previous three equations yields the dependence $p_{\mathrm{sat}} = p_{\mathrm{sat}}(T)$ for the vapor–solid equilibria ($T < T_{\mathrm{t}}$) in the form

$$\ln p_{\mathrm{sat}} = \frac{1}{R}\left(\frac{E_0}{T} + E_1 \ln T + E_2 T\right) + E_3 \tag{21}$$

where the parameters E_0 and E_3 can be calculated by combining ΔH_{mel} and ΔH_{vap} at the triple point temperature T_{t} with the parameters E_1 and E_2

$$E_0 = -(\Delta H_{\mathrm{mel}} + \Delta H_{\mathrm{vap}})_{\mathrm{t}} + E_1 T_{\mathrm{t}} + E_2 T_{\mathrm{t}}^2 \tag{22}$$

$$E_3 = (\ln p_{\mathrm{sat}})_{\mathrm{t}} - \frac{1}{R}\left(\frac{E_0}{T_{\mathrm{t}}} + E_1 \ln T_{\mathrm{t}} + E_2 T_{\mathrm{t}}\right) \tag{23}$$

The simultaneous correlation of vapor–liquid equilibrium data described in the previous section allows the vapor pressure and the enthalpy of vaporization to be calculated at the triple point temperature. For calculating the vapor–solid saturation line it is necessary to also know the enthalpy of melting and the parameters E_1 and E_2 which have to be adjusted from the temperature correlation of differences between the spectroscopic ideal gas heat capacities and calorimetric data for heat capacity of the solid phase.

In many cases one or several transitions between different crystalline phases are observed below the triple point temperature; most transitions are accompanied by a certain heat effect and/or a change in the solid heat capacity. This is reflected by a discontinuous change in the slope of the $p_{\mathrm{sat}} = p_{\mathrm{sat}}(T)$ dependence. In such a case the vapor–solid saturation line has to be constructed stepwise, each section delimited by the neighboring solid–solid transition temperatures (or a solid–solid transition and the triple point temperatures) being described by an independent set of parameters E_1 to E_4. In the first step the parameters of Eq. (21) are established as described above for the interval between the triple point temperature and the nearest solid–solid transition temperature. These parameters are used to determine the vapor pressure and the enthalpy of sublimation corresponding to the lower temperature limit of this interval. In the next steps the same procedure is subsequently repeated for the following neighboring temperature intervals delimited by temperatures where solid–solid transitions occur. Temperature T_t becomes the upper temperature limit of the interval and in Eq. (19), ΔH_{vap} is replaced by the enthalpy of sublimation calculated in the previous step and ΔH_{mel} is substituted by the enthalpy of solid–solid phase transition at the upper temperature.

3. Selection of data and correlation procedure

3.1. Database

Before starting correlations a database has been established including both primary experimental data and smoothed data from the selected secondary sources. The following properties were covered: vapor pressure, enthalpy of vaporization, heat capacity of liquid, heat capacity of ideal gas, melting temperature and solid–solid phase transition temperature, critical properties and acentric factor, enthalpy of melting and enthalpy of solid–solid phase transition, heat capacity of solid. In the development of the database we have used several well-recognized multi- and single-property data collections and compilations. In addition, we have also performed a search of the literature for the most recent data.

Vapor pressure

Compiling all available vapor pressure data was the most important part of our efforts in the development of the database. In the search for the references to original data we have scanned several recognized data collections that included the compilations by Dykyj et al. [10,11] and by Boublik et al. [12], and the tables published at TRC, Texas A&M University [13] and by the ESDU, London [14]. A direct search of the recent primary literature covering the period from 1980 up to the present time did not reveal any new data in addition to those already referred to in the above secondary sources. Data in all literature sources corresponded to the medium pressure range (vapor pressures between 1 and 100 kPa). Included in the database were also the recent unpublished measurements in the low pressure range for three alkylbenzenes [15] (see below).

In selecting the data for the simultaneous correlation we have always preferred the original experimental values; however, in several cases we had to use the recommended data from the TRC Tables and/or the tables published by ESDU. This was the case for 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, and *n*-pentylbenzene where no reliable experimental data were found in the literature. In addition for 1,2,3,4-tetramethylbenzene and *n*-hexylbenzene the experimental data had to be complemented by the smoothed values for extending the temperature interval for vapor pressure. We were not able to obtain any specifications on the primary data which served for establishing recommendations in the above two secondary sources. The smoothed data from TRC Tables are based mainly on unpublished data from the American Petroleum Institute Research Projects 6 and 44, that are unavailable in literature. Similarly, the ESDU recommended data refer to a report by Ambrose [16] that is not accessible to us.

Most of the medium pressure data selected in our study for generating the recommended values were measured at the former National Bureau of Standards (NBS) Washington DC, USA (today's National Institute of Standards and Technology – NIST). These high quality data obtained by ebulliometry were available for 13 compounds from our selection and cover the pressure range from approximately 7 kPa up to about 100 kPa. Most of the data were published in the paper by Forziati et al. [17]. In the case of propylbenzene and isopropylbenzene two different data sets were reported from NBS [17,18] which have both been included in the correlation. In the case of 1,2,3,4-tetramethylbenzene the three data points from the NBS measurements [19] have been supplemented by the data from secondary sources [13,14]. The vapor pressures determined by McDonald et al. [20] at Dow Chemical by a dynamic boiling method were used for isopropyl-4-methylbenzene (*p*-cymene).

Experimental data of uncertain quality were published as a graph for five polymethylbenzenes containing four to six methyl groups by MacDougall and Smith from the University of Minnesota [21]. Measurements were performed by a dynamic technique at pressures ranging typically from 0.5 to 100 kPa. For all three tetramethylbenzenes these data have been discarded as they differed considerably from the other sources [13,14,19] which were mutually consistent. However, the measurements of McDougall and Smith are the only data source for pentamethylbenzene and hexamethylbenzene and had to be used. All the data below the pressure of 7 kPa have been discarded as it was expected that particularly the low vapor pressure values were prone to important errors.

Three from the investigated alkylbenzenes (*n*-butylbenzene, *sec*-butylbenzene and *n*-hexylbenzene) have been measured recently in the Laboratory of Analytical Chemistry at the University Claude Bernard in Lyon, France (the group of Professor Jose). The vapor pressures were determined by a static method over a wide vapor pressure interval ranging from several pascals up to several tens of kilopascals; the data have been presented recently as a scientific seminar [15] and have not yet been published. Similarly, as in our earlier study on *n*-alkanes [5], we have omitted for this source all data points below 50 Pa as they might be subject to important systematic errors. For *n*-butylbenzene and *sec*-butylbenzene we have considered the Lyon's vapor pressures up to about 3 kPa and above this pressure more accurate NBS data were preferred [17]. For *n*-hexylbenzene where no other direct experimental data are available in the medium pressure range the Lyon's vapor pressures have been included up to their upper temperature limit and supplemented by the values from the TRC Tables [13].

Basic information regarding vapor pressure data sets included in the simultaneous correlation are listed in Table 1. The table gives the number of data points, temperature and pressure limits of the data included in the correlation and the expected overall errors σp_{sat} in the vapor pressure at the lower and upper temperature limits of the included data. The expected overall errors were estimated from reported uncertainties in temperature and pressure using Eq. (13). Also presented are the average deviation d and the average percentage deviation d_{r} for the individual data sets in the final fit. They are defined as

$$d = \left(\frac{\sum_{i=1}^{n_x} (p_{\mathrm{sat}}^{\mathrm{exp}} - p_{\mathrm{sat}}^{\mathrm{sm}})_i^2}{n_x} \right)^{1/2} \tag{24}$$

$$d_{\mathrm{r}} = \left(\frac{\sum_{i=1}^{n_x} [(p_{\mathrm{sat}}^{\mathrm{exp}} - p_{\mathrm{sat}}^{\mathrm{sm}})/p_{\mathrm{sat}}^{\mathrm{sm}}]_i^2}{n_x} \right)^{1/2} 100 \tag{25}$$

where n_x denotes the number of data points in the data set.

Enthalpies of vaporization

The enthalpies of vaporization for the studied alkylbenzenes are in most cases available deep below the lower temperature limit of the included vapor pressure data and therefore affect considerably their extrapolation towards the triple point temperature. All references to the experimental data have been taken from the IUPAC compilation on calorimetric enthalpies of vaporization [22]. No new calorimetric measurements have been published in the last decade.

The direct experimental values are available for nine alkylbenzenes; the data for all members of the group were reported only at one temperature (298.15 K) with the exception of *n*-butylbenzene investigated as function of temperature at the Institute of Chemical Technology in Prague [23]. Highly accurate data obtained by adiabatic calorimetry were reported by Osborne and Ginnings from NBS [24] for two propylbenzenes and for four trimethylbenzenes (expected error below 0.1%). Wadsö at the University of Lund [25] studied 1,3,5-trimethylbenzene using a carrier-gas method with a probable error near 0.5%. A similar approach was adopted by Kusano and co-workers at the Miyazaki University, Japan [26,27], who reported ΔH_{vap} for all nine alkylbenzenes and by Fuchs et al. at the University of Houston, Texas [28] who measured enthalpy of vaporization for *iso*-propylbenzene (expected error of data in the both sources is about 1%). Table 2 reviews the included ΔH_{vap} data sets and has analogous a structure to Table 1. The given relative inaccuracies σ_{r} of the measurements were used for adjusting the variance $\sigma^2 \Delta H'$ in Eq. (12).

Heat capacity differences

Heat capacity differences $\Delta C_{\mathrm{vap}}^{\ominus}$ have been generated from the smoothing equations describing the heat capacity of ideal gas and that of the liquid as a function of temperature.

Table 1
Correlated vapor pressures

Compound	Ref.	No. pts.	$T_{\min}$/K	$T_{\max}$/K	$p_{\min}$/Pa	$p_{\max}$/Pa	$\sigma_{\min}$/Pa	$\sigma_{\max}$/Pa	d/Pa	d_r/%
1-Ethyl-2-methylbenzene	[17]	20	354.3	439.3	6.4E + 3	1.0E + 5	4.8	8.0	7.7	0.09
1-Ethyl-3-methylbenzene	[17]	20	351.2	435.5	6.4E + 3	1.0E + 5	4.8	8.0	7.8	0.09
1-Ethyl-4-methylbenzene	[17]	19	351.4	436.1	6.4E + 3	1.0E + 5	4.8	8.0	3.9	0.05
Isopropylbenzene	[18]	20	343.1	426.5	6.4E + 3	1.0E + 5	38.7	38.7	4.1	0.03
	[17]	20	343.3	426.5	6.4E + 3	1.0E + 5	4.8	8.0	5.0	0.02
Propylbenzene	[18]	20	348.8	433.3	6.4E + 3	1.0E + 5	36.0	36.0	4.2	0.02
	[17]	19	348.9	433.4	6.4E + 3	1.0E + 5	4.8	8.0	4.1	0.02
1,2,3-Trimethylbenzene	[17]	19	363.5	450.3	6.4E + 3	1.0E + 5	4.8	8.0	4.8	0.04
1,2,4-Trimethylbenzene	[17]	20	357.9	443.5	6.4E + 3	1.0E + 5	4.8	8.0	6.1	0.07
1,3,5-Trimethylbenzene	[17]	19	354.6	438.9	6.4E + 3	1.0E + 5	4.8	8.0	3.9	0.03
n-Butylbenzene	[17]	17	369.4	457.5	6.4E + 3	1.0E + 5	4.8	8.0	5.6	0.06
	[15]	7	293.6	353.4	1.1E + 2	3.2E + 3	2.1	64.0	13.5	1.78
Isobutylbenzene	[17]	20	359.8	447.0	6.4E + 3	1.0E + 5	4.8	8.0	3.6	0.02
sec-Butylbenzene	[17]	20	360.2	447.5	6.4E + 3	1.0E + 5	4.8	8.0	7.1	0.09
	[15]	5	303.4	343.6	3.6E + 2	3.1E + 3	7.1	62.0	21.6	1.3
tert-Butylbenzene	[17]	19	357.0	443.3	6.4E + 3	1.0E + 5	4.8	8.0	6.7	0.06
Isopropyl-4-methylbenzene	[20]	7	380.2	451.6	1.2E + 4	1.0E + 5	53.0	89.0	59.4	0.07
1,2,3,4-Tetramethylbenzene	[19]	3	392.5	478.2	7.6E + 3	1.0E + 5	34.0	55.0	10.0	0.06
	[14]	4	413.1	473.1	1.6E + 4	9.0E + 4	3.2	17.9	4.7	0.01
	[13]	9	407.8	480.4	1.3E + 4	1.1E + 5	100.0	160.0	21.7	0.07
1,2,3,5-Tetramethylbenzene	[14]	5	393.1	473.1	9.7E + 3	1.1E + 5	19.4	10.6	3.4	0.03
	[13]	9	401.9	473.3	1.3E + 4	1.1E + 5	100.0	160.0	23.3	0.04
1,2,4,5-Tetramethylbenzene	[14]	5	393.1	473.1	1.0E + 4	1.1E + 5	20.1	10.9	3.2	0.03
	[13]	9	400.9	472.1	1.3E + 4	1.1E + 5	100.0	160.0	38.0	0.07
Pentamethylbenzene	[21]	5	433.1	503.2	1.4E + 4	9.7E + 4	150.0	180.0	96.7	0.2
n-Pentylbenzene	[13]	10	393.1	483.2	7.8E + 3	1.1E + 5	100.0	160.0	1.3	0.01
Hexamethylbenzene	[21]	11	443.1	536.7	7.4E + 3	1.0E + 5	150.0	190.0	370.7	1.35
n-Hexylbenzene	[13]	8	369.1	503.2	1.3E + 3	1.1E + 5	100.0	140.0	51.3	0.8
	[15]	17	303.6	462.9	2.3E + 1	4.1E + 4	0.5	810.0	71.6	0.91

Table 2
Correlated enthalpies of vaporization

Compound	Ref.	No. pts.	T_{min}/K	T_{max}/K	p_{min}/Pa	p_{max}/Pa	σ_r/%	d/kJ mol^{-1}	d_r/%
Isopropylbenzene	[24]	1	298.2		6.2E + 2		0.1	0.01	0.02
	[26]	1	298.2		6.2E + 2		1.0	0.40	0.90
	[28]	1	298.2		6.2E + 2		1.0	0.00	0.01
Propylbenzene	[24]	1	298.2		4.6E + 2		0.1	0.03	0.07
	[26]	1	298.2		4.6E + 2		1.0	0.40	0.87
1,2,3-Trimethylbenzene	[24]	1	298.2		2.1E + 2		0.1	0.10	0.20
	[27]	1	298.2		2.1E + 2		1.0	0.19	0.39
1,2,4-Trimethylbenzene	[24]	1	298.2		2.8E + 2		0.1	0.06	0.12
	[27]	1	298.2		2.8E + 2		1.0	0.80	1.6
1,3,5-Trimethylbenzene	[24]	1	298.2		3.3E + 2		0.1	0.12	0.25
	[25]	1	298.2		3.3E + 2		0.5	0.05	0.10
	[26]	1	298.2		3.3E + 2		1.0	0.05	0.10
n-Butylbenzene	[26]	1	298.2		1.5E + 2		1.0	0.95	1.9
	[23]	3	343.2	368.2	2.0E + 3	6.1E + 3	0.5	0.13	0.29
Isobutylbenzene	[26]	1	298.2		2.6E + 2		1.0	0.17	0.36
sec-Butylbenzene	[26]	1	298.2		2.5E + 2		1.0	0.09	0.18
tert-Butylbenzene	[27]	1	298.2		3.0E + 2		1.0	0.10	0.21

The lower temperature limit for inclusion of $\Delta C_{\mathrm{vap}}^{\ominus}$ in the correlation was given by the availability of $C_p^{\ominus}$ data or the triple point temperature, whichever was higher. This limit has never been set below 250 K as the ideal gas heat capacities started in the used literature source (see below) at 273 K and a long extrapolation outside the validity range of parameters becomes unpredictable.

The maximum acceptable temperature for using $\Delta C_{\mathrm{vap}}^{\ominus}$ in the correlation has been set at about 100 K below the normal boiling temperature. At lower temperatures the pVT correction term in Eq. (9) are smaller by at least one order in magnitude compared with the heat capacity difference; then no distortion in the vapor pressure correlation can occur due to uncertainty in the prediction of vapor nonideality. The only exception was hexamethylbenzene where the difference between the melting and the normal boiling temperature is slightly below 100 K; in this special case the upper limit for inclusion of $\Delta C_{\mathrm{vap}}^{\ominus}$ in the correlation has been set to about ($T_{\mathrm{b}} - 70$ K). In most cases the liquid heat capacities (experimental or predicted) were used up to about 300 K and for the investigated alkylbenzenes this temperature was always below ($T_{\mathrm{b}} - 100$ K). The generation of $\Delta C_{\mathrm{vap}}^{\ominus}$ values was performed over the given temperature interval with a step allowing generation of a number of the heat capacity values which was of the same order as the number of experimental vapor pressures.

Parameters of the smoothing equations for the ideal gas heat capacity have been taken from the compilation by Bureš et al. [29]. These parameters are based on the spectroscopic C_p^{go} values reported in the literature [30-32].

Parameters of the smoothing equations for the heat capacity of the liquid have been taken from the NIST/IUPAC compilation on liquid heat capacities by Zábranský et al. [33]. These recommended data were based on several sources of experimental data [34-46].

For several compounds where the experimental heat capacity of the liquid was not available the values were estimated as a function of temperature using a group contribution method proposed by Růžička and Domalski [47,48]. This was the case for 1-ethyl-2-methylbenzene, 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, isobutylbenzene, and n-pentylbenzene. A review of the heat capacity differences included in the simultaneous correlation is presented in Table 3 which has a format similar to Tables 1 and 2.

Vapor-solid and solid-solid equilibrium data

The vapor pressures above the solid phase have been calculated for eight alkylbenzenes with the triple point temperatures above 223 K (see the next section). For these compounds the triple point temperature, enthalpy of melting and heat capacity of solid phase were needed for determining parameters in Eq. (21). In addition the temperature and enthalpy of the solid-solid phase transition together with the heat capacity of solid below the transition temperature were required for 1,2,3-trimethylbenzene, pentamethylbenzene and hexamethylbenzene. All these data were taken from the compilations by Domalski et al. [49,50]. The parameters of the linear relationship characterizing temperature dependence of $\Delta C_{\mathrm{sub}}^{\ominus}$ were obtained by fitting the differences between heat capacity of an ideal gas and that of the solid.

Table 3
Review of heat capacity differences $\Delta C_{\mathrm{vap}}^{\ominus}$ considered for inclusion in the simultaneous correlation

Compound	No. pts.	$T_{\min}$/K	$T_{\max}$/K	$p_{\min}/Pa$	$p_{\max}$/Pa	$\sigma_{\min}$/J K^{-1} mol^{-1}	$\sigma_{\max}$/J K^{-1} mol^{-1}	d/J K^{-1} mol^{-1}	d_r/%
1-Ethyl-2-methylbenzene	11	250.0	300.0	8.1E + 0	3.9E + 2	7.2	6.5	1.32	2.40
1-Ethyl-3-methylbenzene	11	250.0	300.0	9.6E + 0	4.5E + 2	7.1	6.5	1.78	2.89
1-Ethyl-4-methylbenzene	11	250.0	300.0	9.7E + 0	4.5E + 2	7.1	6.5	1.25	2.03
Isopropylbenzene	11	250.0	300.0	1.6E + 1	7.0E + 2	4.4	2.6	0.16	0.26
Propylbenzene	11	250.0	300.0	1.1E + 1	5.2E + 2	4.4	2.6	0.44	0.68
1,2,3-Trimethylbenzene	11	250.0	300.0	4.1E + 0	2.3E + 2	4.3	1.9	0.97	1.69
1,2,4-Trimethylbenzene	11	250.0	300.0	6.0E + 0	3.2E + 2	4.2	1.9	0.94	1.50
1,3,5-Trimethylbenzene	11	250.0	300.0	7.3E + 0	3.7E + 2	3.9	1.8	1.29	2.03
n-Butylbenzene	11	250.0	300.0	2.4E + 0	1.6E + 2	4.7	2.1	1.24	1.77
Isobutylbenzene	11	250.0	300.0	5.5E + 0	2.9E + 2	8.1	9.1	0.46	0.73
sec-Butylbenzene	5	295.0	315.0	2.1E + 2	7.1E + 2	9.0	9.4	3.92	6.20
tert-Butylbenzene	9	250.0	290.0	6.6E + 0	1.7E + 2	5.2	5.8	3.04	5.19
Isopropyl-4-methylbenzene	11	250.0	300.0	4.1E + 0	2.3E + 2	8.1	7.4	0.56	0.94
1,2,3,4-Tetramethylbenzene	9	280.0	320.0	1.2E + 1	2.2E + 2	7.2	7.9	1.91	3.35
1,2,3,5-Tetramethylbenzene	9	256.0	296.0	1.8E + 0	5.9E + 1	5.4	3.0	0.53	0.86
1,2,4,5-Tetramethylbenzene	5	352.0	372.0	1.7E + 3	4.3E + 3	8.3	8.5	1.35	2.42
Pentamethylbenzene	6	330.0	380.0	1.1E + 2	1.7E + 3	8.8	9.3	7.64	16.0
n-Pentylbenzene	6	250.0	300.0	5.6E − 1	5.5E + 1	9.2	8.5	0.48	0.61
Hexamethylbenzene	6	444.0	469.0	7.8E + 3	1.8E + 4	11.8	12.3	6.41	11.0
n-Hexylbenzene	4	293.2	294.7	9.9E + 0	1.1E + 1	10.9	11.0	3.86	5.20

The melting point and triple point temperatures are considered to be identical in this study as the difference is small compared with the scatter of experimental data.

Auxiliary data

The generalized Tsonopoulos method [51] or the Pitzer and Curl correlation [52] have been adopted for the prediction of the second virial coefficient B as a function of temperature, which is necessary for estimating the nonideality correction terms in Eqs. (8) and (9). Because the thermal data were included only at low pressures the pVT terms played quite a minor role in the correlation. The critical temperature, critical pressure, acentric factors ω and dipole moment needed for the prediction of B according to the Tsonopoulos method have been taken from the database of recommended values of physical and chemical properties for pure compounds CDATA [53]. For those alkylbenzenes where the dipole moment was not available in the literature the method of Pitzer and Curl had to be used because it only requires knowledge of T_c, p_c and ω. The same database was used for obtaining the molar liquid volumes (Eqs. (8) and (9)).

3.2. Correlation procedure

Data fitting was performed in three principal steps.

(1) Vapor pressures in the medium pressure range ($p_{sat} > 1$ kPa) were fitted first alone using Eq. (15) where p_0 was put equal to $p_b = 101.325$ kPa and A_0, A_1, A_2 and $T_0 = T_b$ were adjustable parameters. In this way we have obtained information about the scatter of vapor pressures from different sources and obtained the best possible fit in the range where p_{sat} measurements were generally the most reliable. The value of the normal boiling temperature obtained from this fit was considered as final and was not modified in the subsequent simultaneous correlation.

(2) In the next step Eq. (15) was repeatedly used for correlating simultaneously all included vapor pressures and the preselected thermal data (see Tables 2 and 3). Parameters A_0 to A_2 were considered as adjustable and T_0 determined in the previous step was used. The expected errors of the input data (see Tables 1–3) were used for estimating the variances in Eq. (12). First the correlation weighting factors K_H and K_C were set at unity which gave the same weight to all data points regardless of which property they related to. These factors were changed when necessary in order to achieve a quality of p_{sat} fit comparable to that in step (1), while trying to keep the average deviations d of the fit for ΔH_{vap} and $\Delta C_{vap}^{\ominus}$ close to the expected experimental error. The final parameters were used for generating the recommended values characterizing the vapor–liquid saturation line.

(3) For eight alkylbenzenes which had the triple point temperature above the lower temperature limit of the temperature interval where recommended data were generated (223 to 323 K) Eqs. (20)–(23) were used for calculating the vapor pressures above the solid phase at $T < T_t$. For the three compounds where the temperature of a solid–solid phase transition was inside the above temperature interval the procedure was repeated for calculating the second set of parameters of Eq. (21).

4. Results and discussion

Our main objective was to provide the vapor pressures for the studied alkylbenzenes (liquid or solid) at all temperatures which can be encountered in the environment. The region of interest was set as the temperature interval from 223.15 K to 323.15 K (−50 to 50°C).

Recommended vapor pressures relating to the vapor–liquid saturation line are presented as parameters of the Cox equation (Eq. (15)) in Table 4. Three decimal digits for $T_0 = T_b$ are required because of numerical considerations and they do not express the real accuracy. The parameters are valid over the temperature range delimited by the triple point and normal boiling temperatures. The temperature ranges in which vapor pressures and thermal data were used for determining the parameters can be seen in Tables 1–3. The values of the deviations d and d_r in comparison to the expected errors of the data σ or σ_r give information on the quality of the fit and on the consistency of the three properties. It is apparent that the introduction of the thermal properties does not distort the fit of vapor pressures and the thermal data are described in most cases within their experimental error limits.

Three compounds from our selection are solids over the whole interval of interest and five compounds have the triple point temperature inside this interval. The

Table 4
Recommended vapor pressures, parameters of the Cox Eq. (15)

Compound	Parameters				
	A_0	A_1	A_2	T_0/K	p_0/kPa
1-Ethyl-2-methylbenzene	2.78456	−1.262803E−3	9.410677E−7	438.294	101.325
1-Ethyl-3-methylbenzene	2.81763	−1.446970E−3	1.190853E−6	434.445	101.325
1-Ethyl-4-methylbenzene	2.81962	−1.491165E−3	1.254282E−6	435.129	101.325
Isopropylbenzene	2.85207	−1.706020E−3	1.515962E−6	425.526	101.325
Propylbenzene	2.84665	−1.642586E−3	1.426134E−6	432.355	101.325
1,2,3-Trimethylbenzene	2.82406	−1.421010E−3	1.150777E−6	449.228	101.325
1,2,4-Trimethylbenzene	2.83620	−1.514658E−3	1.285609E−6	442.492	101.325
1,3,5-Trimethylbenzene	2.84392	−1.542754E−3	1.334341E−6	437.856	101.325
n-Butylbenzene	2.87402	−1.602294E−3	1.310974E−6	456.418	101.325
Isobutylbenzene	2.83166	−1.524832E−3	1.249214E−6	445.902	101.325
sec-Butylbenzene	2.82114	−1.466446E−3	1.183218E−6	446.448	101.325
tert-Butylbenzene	2.82617	−1.484306E−3	1.183029E−6	442.260	101.325
Isopropyl-4-methylbenzene	2.82209	−1.438828E−3	1.191725E−6	450.259	101.325
1,2,3,4-Tetramethylbenzene	2.82215	−1.237891E−3	8.772850E−7	478.199	101.325
1,2,3,5-Tetramethylbenzene	2.84492	−1.358804E−3	1.033492E−6	471.159	101.325
1,2,4,5-Tetramethylbenzene	2.84193	−1.344622E−3	1.014758E−6	469.956	101.325
Pentamethylbenzene	2.74762	−5.414505E−4	−1.565635E−7	504.978	101.325
n-Pentylbenzene	2.92248	−1.698029E−3	1.367807E−6	478.616	101.325
Hexamethylbenzene	3.16374	−2.473782E−3	2.224502E−6	536.868	101.325
n-Hexylbenzene	2.93255	−1.512145E−3	1.002619E−6	499.267	101.325

Table 5
Parameters of the vapor pressure Eq. (21) (T/K, p/Pa)

Compound	E_0	E_1	E_2	E_3	Temperature range/K
1,2,3-Trimethylbenzene	−9454.9	557.79	−1.4288	−321.49	223.2–230.3
	−56133	73.506	−0.46246	−13.407	230.3–247.8
1,2,4-Trimethylbenzene	−65814	21.096	−0.09877	22.995	223.2–229.3
1,3,5-Trimethylbenzene	−62845	15.640	−0.09497	25.135	223.2–228.4
1,2,3,4-Tetramethylbenzene	−60689	97.541	−0.27652	−27.945	223.2–265.4
1,2,3,5-Tetramethylbenzene	−66825	56.520	−0.18799	0.27278	223.2–248.6
1,2,4,5-Tetramethylbenzene	−76756	8.0437	−0.06685	30.8487	273.2–352.1
Pentamethylbenzene	−63130	103.91	−0.24194	−35.031	223.2–296.8
	−61911	116.18	−0.29188	−42.139	296.8–328.2
Hexamethylbenzene	−66971	125.29	−0.23118	−52.303	223.2–383.7
	−58215	127.73	−0.19007	−58.692	383.7–438.7

parameters of Eq. (21) describing vapor pressures relating to the vapor–solid saturation line are listed in Table 5. The lower and upper temperature limit of validity is always the temperature of 225.15 K and the triple point temperature, respectively. Two sets of parameters are given for three compounds where a solid–solid phase transition is reported between 223.15 and 323.15 K.

The vapor pressures generated from Eqs. (15) and (21) using the parameters in Table 4 and 5 are tabulated between 223.15 and 323.15 K with a step of 10 K in Table 6. Vapor pressures corresponding to the vapor–solid saturation line are printed in italics. The vapor pressures for undercooled liquid obtained by extrapolation from Eq. (15) below the triple point temperature are also listed. The ratio of vapor pressure of solid to that of undercooled liquid is called the ideal solubility [54] and gives the solubility of a compound at a given temperature in an ideal solution.

Recommended values of vapor pressure, enthalpy of vaporization, enthalpy of sublimation and heat capacity differences $\Delta C^{\ominus}_{\mathrm{vap}}$ and $\Delta C^{\ominus}_{\mathrm{sub}}$ at the triple point temperature are summarized for eight alkylbenzenes melting above 223.15 K in Table 7. Table 8 lists recommended values of vapor pressure, enthalpy of vaporization or sublimation, and the heat capacity difference $\Delta C^{\ominus}_{\mathrm{vap}}$ or $\Delta C^{\ominus}_{\mathrm{sub}}$ for all 20 alkylbenzenes at 298.15 K.

The estimated uncertainty of recommended vapor pressure at 298.15 K is better than 10% for all compounds that are liquid at this temperature. The uncertainty increases at the triple point temperature but stays within the 10% limit for all compounds having the triple point temperature above 223.15 K. Only for pentamethylbenzene is the uncertainty at the triple point temperature slightly above 10%. We expect that the uncertainty of recommended sublimation pressures (1,2,4,5-tetramethylbenzene, pentamethylbenzene, and hexamethylbenzene) will roughly double compared to that at the triple point.

Table 6
Recommended vapor pressures in the range from 223.15 K to 323.15 K

Compound	p_{sat}/Pa										
	223.15 K	233.15 K	243.15 K	253.15 K	263.15 K	273.15 K	283.15 K	293.15 K	303.15 K	313.13 K	323.15 K
1-Ethyl-2-methylbenzene	0.442	1.426	4.134	10.90	26.45	59.61	125.8	250.4	472.8	851.8	1471.
1-Ethyl-3-methylbenzene	0.522	1.689	4.895	12.90	31.23	70.18	147.6	292.6	550.4	987.1	1697.
1-Ethyl-4-methylbenzene	0.532	1.716	4.966	13.06	31.55	70.75	148.5	293.8	551.5	987.2	1693.
Isopropylbenzene	0.949	2.999	8.496	21.88	51.82	113.9	234.6	455.7	840.1	1478.	2493.
Propylbenzene	0.610	1.973	5.711	15.00	36.20	80.99	169.5	334.3	625.1	1114.	1904.
1,2,3-Trimethylbenzene	*0.118* [a]	*0.522*	*1.884*	5.606	14.17	33.12	72.25	148.2	287.5	531.0	937.9
	0.195 [b]	0.666 [b]	2.031 [b]								
1,2,4-Trimethylbenzene	*0.245*	0.993	2.975	8.071	20.07	46.21	99.36	201.0	385.1	702.4	1226.
	0.296 [b]										
1,3,5-Trimethylbenzene	*0.328*	1.228	3.648	9.825	24.26	55.49	118.6	238.5	454.4	824.6	1433.
	0.369 [b]										
n-Butylbenzene	0.101	0.365	1.171	3.379	8.883	21.50	48.39	102.0	202.9	383.0	689.8
Isobutylbenzene	0.271	0.913	2.741	7.453	18.57	42.81	92.14	186.5	357.6	652.5	1139.
sec-Butylbenzene	0.266	0.891	2.671	7.253	18.05	41.60	89.54	181.3	347.7	634.9	1109.
tert-Butylbenzene	0.334	1.109	3.296	8.878	21.93	50.18	107.3	215.8	411.3	746.7	1298.
Isopropyl-4-methylbenzene	0.193	0.659	2.007	5.530	13.96	32.58	70.97	145.4	281.8	519.9	917.5
1,2,3,4-Tetramethylbenzene	*0.0097*	*0.0474*	*0.201*	*0.759*	*2.564*	6.801	16.03	35.33	73.36	144.3	270.4
	0.0246 [b]	0.0943 [b]	0.319 [b]	0.969 [b]	2.678 [b]						
1,2,3,5-Tetramethylbenzene	*0.0178*	*0.0896*	*0.393*	1.358	3.713	9.337	21.79	47.56	97.79	190.6	353.9
	0.0356 [b]	0.135 [b]	0.452 [b]								
1,2,4,5-Tetramethylbenzene	*8.4×10^{-4}*	*4.8×10^{-3}*	*0.0233*	*0.1002*	*0.3838*	*1.326*	*4.181*	*12.13*	*32.68*	*82.28*	*194.9*
	0.0387 [b]	0.146 [b]	0.486 [b]	1.454 [b]	3.962 [b]	9.926 [b]	23.09 [b]	50.26 [b]	103.1 [b]	200.4 [b]	371.3 [b]
Pentamethylbenzene	*3.5×10^{-4}*	*1.9×10^{-3}*	*9.3×10^{-3}*	*0.0397*	*0.150*	*0.515*	*1.612*	*4.641*	*12.19*	*29.58*	*67.44*
	0.0302 [b]	0.0126 [b]	0.0464 [b]	0.154 [b]	0.460 [b]	1.265 [b]	3.218 [b]	7.639 [b]	17.03 [b]	35.89 [b]	71.83 [b]
n-Pentylbenzene	0.0171	0.0698	0.249	0.794	2.280	5.981	14.48	32.66	69.07	137.9	261.7
Hexamethylbenzene	*2.0×10^{-6}*	*1.4×10^{-5}*	*8.2×10^{-5}*	*4.2×10^{-4}*	*1.9×10^{-3}*	*7.8×10^{-2}*	*0.0289*	*0.0974*	*0.303*	*0.873*	*2.353*
	5.2×10^{-5} [b]	3.3×10^{-4} [b]	1.8×10^{-3} [b]	8.1×10^{-3} [b]	0.0319 [b]	0.112 [b]	0.350 [b]	0.995 [b]	2.598 [b]	6.283 [b]	14.18 [b]
n-Hexylbenzene	0.0274	0.0125	0.0497	0.174	0.547	1.559	4.076	9.869	22.30	47.38	95.20

[a] Sublimation vapor pressure values are given in italics. [b] Hypothetical undercooled liquid.

Table 7
Recommended values of vapor pressure, enthalpy of vaporization and heat capacity difference at the triple point

Compound	T_t/K	p_{sat}/Pa	ΔH_{vap}/kJ mol^{-1}	ΔH_{sub}/kJ mol^{-1}	$\Delta C^{\ominus}_{vap}$/J K^{-1} mol^{-1}	$\Delta C^{\ominus}_{sub}$/J K^{-1} mol^{-1}
1,2,3-Trimethylbenzene	247.8	3.30	51.97	60.15	−60.52	−41.09
1,2,4-Trimethylbenzene	229.3	0.634	52.27	65.46	−63.42	−24.20
1,3,5-Trimethylbenzene	228.4	0.706	51.95	61.46	−64.14	−27.74
1,2,3,4-Tetramethylbenzene	265.4	3.33	55.87	67.10	−58.10	−49.23
1,2,3,5-Tetramethylbenzene	248.6	0.833	56.32	69.26	−62.42	−36.95
1,2,4,5-Tetramethylbenzene	352.1	1760.	49.96	71.30	−54.83	−39.03
Pentamethylbenzene	328.2	100.	57.93	68.60	−45.80	−75.41
Hexamethylbenzene	438.7	6520.	57.03	77.67	−67.43	−39.03

Table 8
Recommended values of vapor pressure, enthalpy of vaporization and heat capacity difference at 298.15 K

Compound	p_{sat}/Pa	ΔH_{vap}/kJ mol^{-1}	$\Delta C^{\circ}_{\mathrm{vap}}$/J K^{-1} mol^{-1}
1-Ethyl-2-methylbenzene	346.2	46.94	−53.23
1-Ethyl-3-methylbenzene	403.8	46.62	−57.51
1-Ethyl-4-methylbenzene	405.0	46.47	−58.19
Isopropylbenzene	622.5	45.13	−63.11
Propylbenzene	460.0	46.19	−62.55
1,2,3-Trimethylbenzene	207.8	48.96	−58.49
1,2,4-Trimethylbenzene	280.0	47.99	−59.97
13,5-Trimethylbenzene	331.3	47.58	−60.24
n-Butylbenzene	144.9	50.78	−66.95
Isobutylbenzene	259.9	48.04	−61.32
sec-Butylbenzene	252.7	48.07	−59.59
tert-Butylbenzene	299.9	47.61	−60.52
Isopropyl-4-methylbenzene	203.7	48.87	−58.41
1,2,3,4-Tetramethylbenzene	51.27	53.96	−57.66
1,2,3,5-Tetramethylbenzene	68.68	53.25	−60.92
1,2,4,5-Tetramethylbenzene [a]	20.09	73.21 [b]	−60.40
Pentamethylbenzene [a]	7.63	70.60 [b]	−41.98
n-Pentylbenzene	47.85	55.33	−75.69
Hexamethylbenzene [a]	0.17	83.78 [b]	−125.49
n-Hexylbenzene	14.96	60.24	−78.01

[a] Values for solid–vapor equilibrium. [b] Enthalpy of sublimation.

The estimated uncertainty of enthalpies of vaporization at 298.15 K is below 2% for all alkylbenzenes from our selection that are liquid at this temperature.

Table 9 shows the percentage differences between the vapor pressures and enthalpies of vaporization calculated from the simultaneous correlation and those obtained from the Antoine equation

$$\ln p_{\mathrm{sat}} = A + \frac{B}{T + C} \tag{26}$$

which is widely used for extrapolations in the environmental literature. The comparison was performed for the triple point temperature (provided T_{t} is above 225.15 K) and for 298.15 K. We have determined the parameters of the Antoine equation using the data above the pressure of 10 kPa from the same literature sources as for the simultaneous correlation; the corresponding temperature ranges are also listed in Table 9. The extrapolation below the triple point temperature was carried out following the same procedure as for producing the recommended data. The results clearly demonstrate that a long extrapolation of vapor pressure data from the medium pressure range by a simple Antoine equation may lead to substantial errors especially in those cases where the experimental data are of low quality. While the agreement is still reasonable at conditions where the extrapolated

Table 9
Comparison of extrapolations from the medium pressure range using the Antoine equation with the results from the simultaneous correlation

Compound	Medium pressure range		Triple point		298.15 K	
	T_{min}/K	T_{max}/K	dp_{sat}/% [a]	$d\Delta H_{vap}$/% [a]	dp_{sat}/%	$d\Delta H_{vap}$/%
1-Ethyl-2-methylbenzene	366	438	n.a. [b]	n.a.	−5.2	3.4
1-Ethyl-3-methylbenzene	363	434	n.a.	n.a.	−3.8	2.6
1-Ethyl-4-methylbenzene	363	435	n.a.	n.a.	−3.1	2.3
Isopropylbenzene	355	426	n.a.	n.a.	−1.9	1.6
Propylbenzene	360	432	n.a.	n.a.	−2.5	2.0
1,2,3-Trimethylbenzene	375	449	−25.5	9.5	−4.7	2.9
1,2,4-Trimethylbenzene	369	442	−35.3	12.0	−3.4	2.3
1,3,5-Trimethylbenzene	366	438	−33.0	11.2	−2.7	2.0
n-Butylbenzene	381	457	n.a.	n.a.	−5.9	3.5
Isobutylbenzene	371	446	n.a.	n.a.	−4.5	3.0
sec-Butylbenzene	372	447	n.a.	n.a.	−4.9	3.1
tert-Butylbenzene	369	442	n.a.	n.a.	−4.7	3.1
Isopropyl-4-methylbenzene	380	450	n.a.	n.a.	−3.7	2.5
1,2,3,4-Tetramethylbenzene	393	478	−30.3	11.1	−12.3	5.9
1,2,3,5-Tetramethylbenzene	393	471	−37.6	12.9	−9.2	4.7
1,2,4,5-Tetramethylbenzene	393	470	−1.1	1.2	1.7 [c]	−1.8 [c]
Pentamethylbenzene	433	503	−32.5	16.8	−51.0 [c]	11.0 [c]
n-Pentylbenzene	403	480	n.a.	n.a.	−8.4	4.4
Hexamethylbenzene	453	537	1.5	−2.0	65.3 [c]	−4.7 [c]
n-Hexylbenzene	422	500	n.a.	n.a.	−10.9	6.2

[a] $dX = 100\,(X^{\mathrm{Antoine}} - X^{\mathrm{SimCor}})/X^{\mathrm{SimCor}}$, where $X = p_{sat}$, ΔH_{vap}. [b] Does not apply; calculation was not performed at $T_t < 223$ K. [c] Values for vapor–solid equilibrium.

vapor pressures are several hundreds of pascals, the simple extrapolation generally fails at lower pressures.

Experimental vapor pressures for solid 1,2,4,5-tetramethylbenzene, pentamethylbenzene and hexamethylbenzene were reported by Colomina et al. [55] who employed the effusion technique for measuring in the pressure range from about 0.05 Pa to 40 Pa. In addition two independent data sets are available for solid hexamethylbenzene at somewhat higher temperatures determined by two different techniques: a saturation method (Overberger et al. [56]) and a static method (Ambrose et al. [57]). These two latter sources exhibit an excellent consistency and also agree reasonably well with the data of Colomina et al. [55] at their lower temperature limit. A comparison of the above experimental vapor pressures with our results and with the extrapolation using exclusively Antoine fit of medium pressure data is illustrated in Figs. 1–4. It is obvious that the simultaneous correlation agrees reasonably with the experimental data and the Antoine equation fails completely in long extrapolation for pentamethyl- and hexamethylbenzenes.

The influence of the change in the vapor pressure of a chemical on its distribution in the environment was examined using a simple six-compartment model of a unit

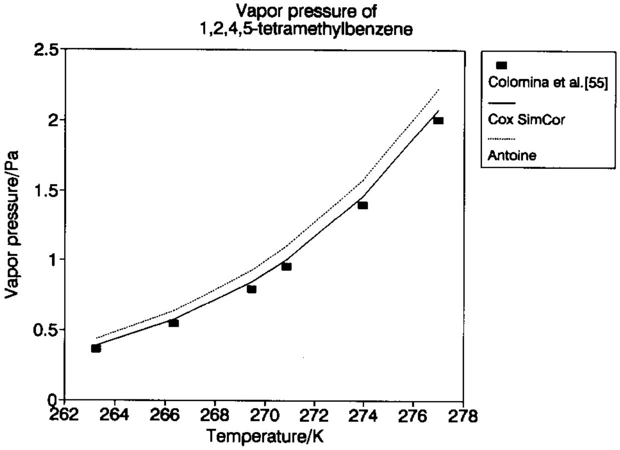

Fig. 1. Vapor pressure of 1,2,4,5-tetramethylbenzene.

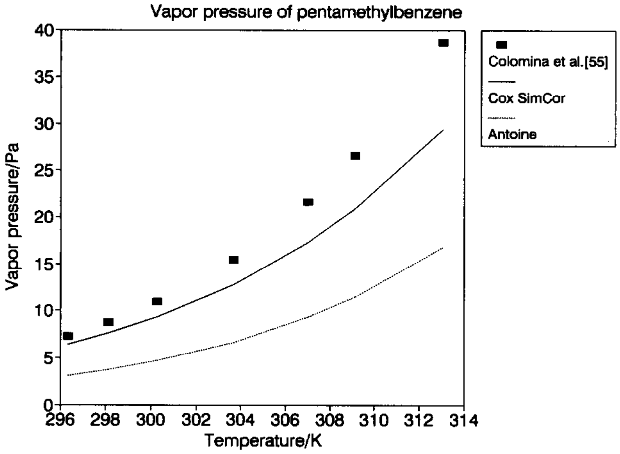

Fig. 2. Vapor pressure of pentamethylbenzene.

world developed by Mackay [58]. In this model, partitioning of a chemical into six environmental media (air, water, soil, sediment, suspended sediment, and fish) is calculated assuming that there is no net accumulation or depletion of a chemical due to a reaction or flows in air or water. 1,2,4,5-Tetramethylbenzene was selected for the illustrative calculation as the vapor pressure of the solid phase at 298.15 K calculated in this work (20.1 Pa) differed significantly from the recommended value given by Mackay et al. [59] (66 Pa). It should be noted, however, that the latter source incorrectly reports this value as a liquid phase vapor pressure despite the fact that the melting temperature of the compound is 377.4 K. When comparing

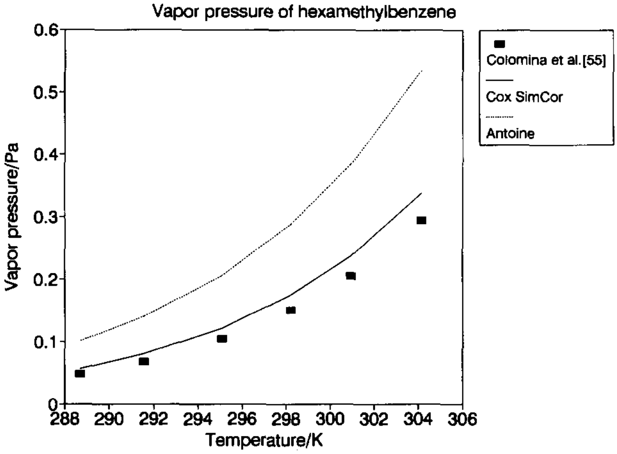

Fig. 3. Vapor pressure of hexamethylbenzene.

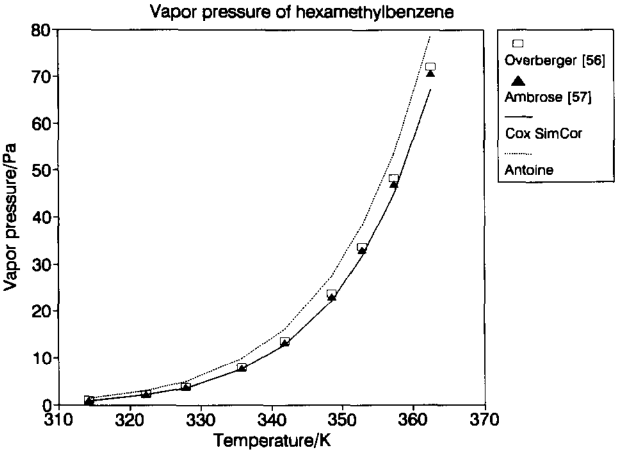

Fig. 4. Vapor pressure of hexamethylbenzene.

concentrations of 1,2,4,5-tetramethylbenzene in the six compartments of the environment obtained by using the above two values of the vapor pressure we found that concentrations in water, sediment, and fish differed by more than one order of magnitude. In all three compartments the concentrations were higher when using the vapor pressure calculated in this work.

Acknowledgments

The authors are grateful to ESDU International plc, for the donation of ESDU tables, Vapour pressure and critical points of liquids. Part 3A: C_6 to C_{10} alkylbenzenes, Item 86012. This project was supported by the Mission Interministerielle pour la Coopération avec l'Europe Centrale et Orientale (MICECO), Environmental program France–Czech Republic. One of the authors (K.R.) acknowledges support for his stay in France through the PECO grant "Go West" ERB3510PL921823/10078 of the Commission of the European Communities.

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