



Weaving a web of reliable thermochemistry around lignin building blocks: phenol, benzaldehyde, and anisole

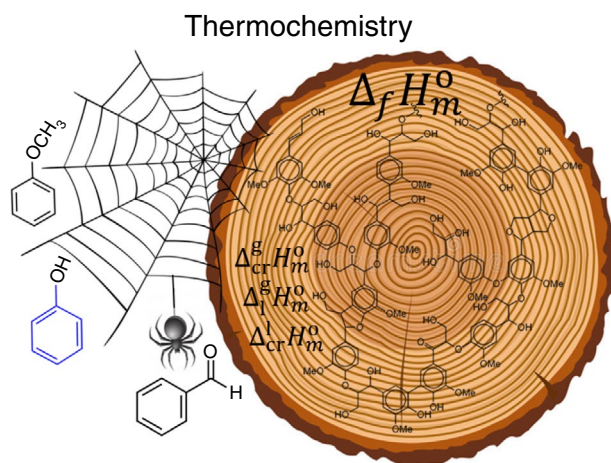
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Abstract

Substituted benzenes such as phenol, benzaldehyde, and anisole are the simplest fragments from the lignin separation feedstocks. We have collected available primary experimental results on vapour pressures, enthalpies of phase transition, and enthalpies of combustion of phenol, benzaldehyde, and anisole. The resulting data on the gas-phase standard molar enthalpies of formation were validated using the quantum chemical method G4. The consistent sets of evaluated thermodynamic data are essential for calculating the energy balances of lignin conversion in the value-added chemicals and materials.

Graphic abstract



Keywords Lignin · Substituted benzenes · Thermochemical properties · Quantum-chemical calculations

Introduction

Lignin is the most abundant polymer material that is based on aromatic units in nature. Lignin is broadly used either directly or chemically modified, as component for composites and copolymers, dispersant agent for pesticides, emulsifier, etc.

Millions of tons of lignin are produced in the paper industry every year. Despite the natural abundance of lignin, valorisation of this polymer into more useful chemicals has proven to be a major challenge. Lignin is comprised by a number of different subunits and chemical bonds, and this inherent complexity makes it difficult to achieve selectivity in chemical conversions. At least three basic monomer units (phenol, benzaldehyde, and anisole) can be identified [1] in the network of the lignin structure (see Fig. S1). For value-added applications of lignin to be improved, medium- and long-term conversion technologies must be developed, especially for the preparation of low molecular weight compounds as an alternative to the petrochemical industry [2]. In order to

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develop the valorisation technologies and understand the energetics and mechanisms that control the monomer formation and distribution, reliable thermodynamic data have to be collected and evaluated for building blocks that result from the thermal conversion of lignin. The fundamental properties such as enthalpies of phase transitions (vaporisation, sublimation, and fusion) and enthalpies of formation are used in the design and optimisation of chemical processes involved in lignin valorisation technologies.

The thermochemical studies of phenol (CAS 108–95-2), benzaldehyde (CAS 100–52-7), and anisole (or methoxybenzene, CAS 100–66-3) have been a popular endeavour since the beginning of the quantitative thermochemistry [3, 4]. Surprisingly, some hidden inconsistencies have been discovered in the recent literature even for these basic molecules. For example, Simões et al. [5] pointed to significant discrepancies in the literature data for the enthalpy of formation of gaseous anisole. This controversy affects the reliability of the enthalpy of formation of the phenoxy radical and of the gas-phase O–H bond dissociation enthalpy in phenol. The latter enthalpy is essential to understand the chemical and biochemical behaviour of phenolic compounds in general. However, despite numerous experimental and computational studies on phenol, its gaseous enthalpy of formation also still remains controversial [6].

This article is a continuation of a series of related previous works on “weaving a network of reliable thermochemistry around lignin building blocks [7, 8]” and also continues our earlier systematic studies [9–12] to investigate model compounds relevant to valorisation of biomass. In this paper, we collected and evaluated available in the literature results on vapour pressures, phase transitions, and enthalpies of formation of three basic lignin building blocks: phenol, benzaldehyde, and anisole. A benchmark quality data sets of the thermodynamic properties for these compounds were achieved through careful analysis of available primary experimental results. The recommended data are important for the downstream processing of lignin-derived feedstock into end products.

Vapour pressures’ data treatment

The experimental absolute vapour pressures, p_i and temperature dependences available in the literature were fitted with the following equation [13]:

$$R \ln(p_i/p_{\text{ref}}) = a + \frac{b}{T} + \Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}} \times \ln\left(\frac{T}{T_0}\right) \quad (1)$$

where $\Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}}$ is the difference of the molar heat capacities of the gas and the crystal (or liquid) phases, respectively, a and b are adjustable parameters, $R = 8.31446 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the molar gas constant, and the reference pressure $p_{\text{ref}} = 1 \text{ Pa}$.

The arbitrary temperature T_0 given in Eq. (1) was chosen to be $T_0 = 298.15 \text{ K}$.

Experimental vapour pressures have been used to obtain the enthalpies of sublimation/vaporisation of vanillins using the following equation:

$$\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\text{o}}(T) = -b + \Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}} \times T \quad (2)$$

Experimental vapour pressures’ temperature dependences were also used to derive the sublimation/vaporisation entropies at temperatures T by using the following equation:

$$\Delta_{\text{cr,l}}^{\text{g}} S_{\text{m}}^{\text{o}}(T) = \Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\text{o}}/T + R \times \ln(p_i/p^{\text{o}}) \quad (3)$$

with $p^{\text{o}} = 0.1 \text{ MPa}$. The combined uncertainties of the sublimation/vaporisation enthalpies include uncertainties from the experimental conditions, uncertainties in vapour pressure and uncertainties due to the temperature adjustment to $T = 298.15 \text{ K}$ as described elsewhere [14, 15].

Quantum-chemical calculations

Theoretical values of the gas-phase standard molar enthalpies of formation of substituted benzenes were calculated by using quantum-chemical calculations. We used the composite G4 [16] method available in the Gaussian 09 software package [17] for calculations of enthalpies H_{298} , which were finally converted to the $\Delta_{\text{f}}H_{\text{m}}^{\text{o}}(\text{g})$ -values by using the atomisation procedure. For quantum-chemical calculations, we used the most stable conformer of each substituted benzene. The necessary details can be found in Supporting Information. More details can be found elsewhere [18]. The well-established assumption “rigid rotator”- “harmonic oscillator” was used for the quantum-chemical calculations.

It is already well established that the quantum chemical composite methods are nowadays a valuable tool for obtaining the *theoretical* $\Delta_{\text{f}}H_{\text{m}}^{\text{o}}(\text{g}, 298.15)$ -values with a “chemical accuracy”. The latter is conventionally defined at the level of 4–5 kJ mol^{-1} [18]. Since the available thermochemical data for phenol, benzaldehyde, and anisole need to be evaluated, it is reasonable to use the quantum-chemical calculations to establish the consistency and to support the reliability of the results derived in this work. A correspondence between the *theoretical* and *experimental* $\Delta_{\text{f}}H_{\text{m}}^{\text{o}}(\text{g}, 298.15 \text{ K})$ -values provides a valuable evidence of the data mutual consistency.

Thermochemistry of phenol

Dorofeeva and Ryzhova [6] have demonstrated just recently that the commonly accepted experimental value of the gas-phase standard molar enthalpy of formation of

phenol $\Delta_f H_m^o(g)_{\text{exp}} = (-96.4 \pm 0.6 \text{ kJ mol}^{-1})$ [4, 19] was noticeably different from the G4 calculated value $\Delta_f H_m^o(g)_{\text{G4}} = (-91.8 \pm 2.5 \text{ kJ mol}^{-1})$. This discrepancy was considerably larger than the error assigned to the experimental result, and it was also inconsistent with the error expected from the computational method [6]. They suggested that the G4 value should be preferred over the available experimental value [4, 19], because the quantum-chemical result for phenol was highly consistent with high accuracy $\Delta_f H_m^o(g)_{\text{exp}}$ values of 36 different species with well-established thermochemistry, which were involved in atomisation, isodesmic, and isogyric reactions. In addition, the G4 result for phenol was in internal consistency with the $\Delta_f H_m^o(g)_{\text{exp}}$ -values of 13 closely related substituted phenols [6]. Given the convincing ambiguity of the $\Delta_f H_m^o(g)_{\text{exp}}$ result of phenol, it makes sense to analyse and re-evaluate the available primary experimental data. Indeed, according to the textbook equation for the gas-phase enthalpy of formation

$$\Delta_f H_m^o(g)_{\text{exp}} = \Delta_f H_m^o(\text{cr or l}) + \Delta_{\text{cr,l}}^g H_m^o \quad (4)$$

it is reasonable to evaluate the data sets of $\Delta_f H_m^o(\text{cr})$, $\Delta_{\text{cr,l}}^g H_m^o$ and $\Delta_{\text{cr,l}}^g H_m^o$ separately.

Evaluation of $\Delta_f H_m^o(\text{cr})$ -values. Combustion experiments with the phenol are challenging because it is hygroscopic and tends to be oxidised by air or oxygen [20]. We have compiled available calorimetric results for phenol in Table 1. One of the first compendiums of thermochemical data by Kharasch reported in 1929 [3] evaluated combustion experiments (see Table 1) performed by Stohmann and Langbein from 1892 [21], as well as six combustion enthalpies from earlier sources cited therein. Although the combustion enthalpy of phenol reported by Barker in 1925 [22] was consistent with previous results [3], that paper was presumably overlooked by Kharasch [3]. Badoche [23] reported in 1941 the combustion energy of phenol at 290 K. Cox and Pilcher [4] have corrected his combustion result from 290 to 298.15 K, applied correction to the standard state, and

assigned a fair uncertainty interval of $\pm 3.2 \text{ kJ mol}^{-1}$ for the combustion enthalpy (see Table 1). Papers from nineteenth-century measurements collated by Kharasch [3] and measurements reported by Barker [22] contain so little experimental information that detailed uncertainties assignment is hardly possible. Hence, for the sake of comparison, we therefore followed the suggestion of Cox and Pilcher [4], which was applied to the combustion results of Badoche [23], and we assigned the conservative uncertainty intervals of $\pm 3.2 \text{ kJ mol}^{-1}$ (see Table 1) also for combustion enthalpies given in references [3, 22] (see Table 1).

Later, the combustion enthalpy of phenol was measured in the Stanford University as a part of a comprehensive program of thermochemical data for organic compounds containing oxygen [24] (see Table 1). However, also in this case, only final combustion and formation enthalpies were reported in the article. Nevertheless, based on our experience with experimental work from that laboratory, the result for phenol can be regarded as reliable. For example, the enthalpy of formation for para-benzoquinone reported in the same paper [24] agrees very closely with the result measured in the renowned Physical Chemistry Laboratory (Oxford) [25].

The latest combustion enthalpy of phenol was reported in 1960 by Andon et al. [26] from the National Chemical Laboratory of UK. This result (see Table 1) is in good agreement with Parks et al. [24] and Badoche [23], but it is somewhat more negative in comparison with those from Barker [22] and Kharasch [3]. The study by Andon et al. [26] included careful thermochemical work not only on phenol, but also on cresols and xylenols. The study of phenol seems to be of impeccable quality, but they reported few disconcerting observations. The aqueous bomb contents from the combustion of phenol (and also of ortho- and meta-cresol) had a very pale yellow colour. The bomb liquors from para-cresol and the xylenols were colourless. Spectroscopic examination suggested that the colour of the yellow solutions was due to traces of nitrophenols as an evidence of partial combustion.

Table 1 Phenol: compilation of enthalpies of formation $\Delta_f H_m^o(\text{cr})$ available in the literature (kJ mol^{-1})

Compound	$\Delta_c H_m^o(\text{cr})$	$\Delta_f H_m^o(\text{cr})$	$\Delta_{\text{cr,l}}^g H_m^o$ ^a	$\Delta_f H_m^o(g)_{\text{exp}}$	$\Delta_f H_m^o(g)_{\text{G4}}$ ^b
Phenol (cr)	-3066.1 ± 3.2 [22]	-152.5 ± 3.3			
	-3064.6 ± 3.2 [3]	-154.0 ± 3.3			
	-3053.9 ± 3.2 [23]	-164.7 ± 3.3			
	-3056.0 ± 1.2 [24]	-162.6 ± 1.5			
	-3053.4 ± 3.0 [26]	-165.2 ± 3.1			
			-161.1 ± 1.1	68.6 ± 0.5	-92.5 ± 1.2

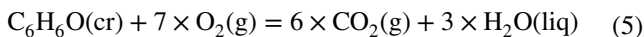
^aEvaluated sublimation enthalpy from Table 3

^bTheoretical enthalpies of formation calculated using the G4 method according to atomisation procedure

Uncertainties in this table are the expanded uncertainty (0.95 level of confidence, $k=2$). The uncertainties of the available combustion results were re-calculated in this work according to the modern conventional procedure (see details in electronic supporting information)

Their presence in the calculation of the enthalpy of combustion was not taken into account. In addition, tiny soot spots were formed in some experiments [26]. To reflect these disconcerting observations, the uncertainties of the enthalpy of combustion for phenol reported by Andon et al. [26] were doubled in accordance with standard thermochemical practice.

The standard molar enthalpies of formation $\Delta_f H_m^o(\text{cr})$ of phenol were derived from the standard molar enthalpies of combustion $\Delta H_m^o(\text{cr})$ evaluated for every literature source (see Table 1). Combustion results were referenced to the reaction:



The $\Delta_f H_m^o(\text{cr})$ -values of phenol were obtained (see Table 1) applying the Hess's law to Eq. (5) with the help of the current standard molar enthalpies of formation of $\text{H}_2\text{O}(\text{liq})$ and $\text{CO}_2(\text{g})$ recommended by CODATA [27]. In order to get more confidence, all five $\Delta_f H_m^o(\text{cr})$ -values of phenol were averaged by using uncertainty as the weighing factor. The weighted average value $\Delta_f H_m^o(\text{cr}, 298.15 \text{ K}) = -161.1 \pm 1.1 \text{ kJ mol}^{-1}$ derived in this way can be now used for calculation of the gas-phase enthalpy of formation according to Eq. (4).

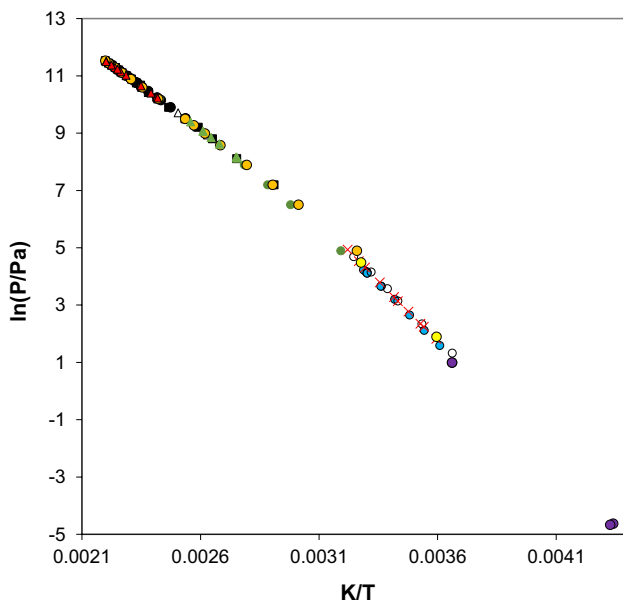


Fig. 1 Temperature dependence of vapour pressures for the solid and liquid phenol: blue round—transpiration [36]; red cross—transpiration [31]; ○—static [31]; black round—ebullimetry [31]; ■—ebullimetry [44]; green round—ref. [40]; △—ref. [42]; yellow round—static [32]; dark yellow round—ebullimetry [43]; red triangle—static [41]; purple round—Knudsen effusion method [33]; green triangle—ebullimetry [45]

Evaluation of vapour pressures over the solid phenol and $\Delta_{\text{cr}}^g H_m^o$ -values. There are eight articles (see Fig. 1) dealing with vapour pressure temperature dependences measured over the crystalline sample of phenol [29–36], including our own measurements by using the transpiration method [36]. The comprehensive compilation by Stephenson and Malanowsky [35] contains a set of Antoine's equation coefficients with no specified origin of these data. The available vapour pressures are given in Fig. 1. As it can be seen, the agreement of data from various methods is sufficient, except for the data set measured by using the Knudsen method [33]. Unfortunately, the experimental details in the original work are scarce to explain the disagreement observed. Nevertheless, the consistency of other data sets [31, 36] is sufficient to combine them and develop a general approximation equation. For this purpose, we used the Clarke and Glew equation [37]:

$$R \times \ln\left(\frac{p}{p^o}\right) = -\frac{\Delta_{\text{cr,l}}^g G_m(\theta)}{\theta} + \Delta_{\text{cr,l}}^g H_m^o(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{\text{cr,l}}^g C_{p,m}^o(\theta)\left(\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right) \quad (6)$$

where p is the absolute vapour pressure at the temperature T , p^o is an arbitrary reference pressure ($p^o = 10^5 \text{ Pa}$ in this work), θ is an arbitrary reference temperature ($\theta = 298.15 \text{ K}$ in this work), R is the molar gas constant, $\Delta_{\text{cr,l}}^g G_m(\theta)$ is the difference in the molar Gibbs energy between the gas and crystal (or liquid) at the selected reference temperature, $\Delta_{\text{cr,l}}^g H_m^o$ is the difference in the molar enthalpy between the gas and the crystal (or liquid), and $\Delta_{\text{cr,l}}^g C_{p,m}^o(\theta)$ is the difference in the molar heat capacity at constant pressure between the gas and the crystal (or liquid). An advantage of the Clarke and Glew equation [37] is that the fitting coefficients (in contrast to Eq. (1)) are directly related to the thermodynamic functions of vaporisation. The set of experimental absolute vapour pressures is given in Table S1 and the coefficients of Eq. (6) are listed in Table 2.

Taking into account that the sublimation temperature range is not too large, the $\Delta_{\text{cr}}^g C_{p,m}^o$ -value cannot be applied as adjustable parameter of Eq. (6). The value $\Delta_{\text{cr}}^g C_{p,m}^o = -19.8 \text{ J mol}^{-1} \cdot \text{K}^{-1}$ was calculated with the help

Table 2 Thermodynamics functions of sublimation/vaporization of phenol ($T = 298.15 \text{ K}$)

State	T -range K	$\Delta_{\text{I,cr}}^g G_m^o$ kJ mol ⁻¹	$\Delta_{\text{I,cr}}^g H_m^o$ kJ mol ⁻¹	$-\Delta_{\text{I,cr}}^g C_{p,m}^o$ J mol ⁻¹ ·K ⁻¹
Crystal	277.2–310.6	19.24 ± 0.03	68.4 ± 0.8	19.8
Liquid	332.4–455.1	18.44 ± 0.09	58.3 ± 0.7	70 ± 7

Uncertainties in this table are the standard uncertainty (0.683 level of confidence, $k = 1$)

of empirical equation suggested by Chickos and Acree [38], based on the experimental heat capacity $C_{p,m}^o(\text{cr}) = 127.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ [39]. The coefficients of Eq. (6) can be now used for the interpolation of vapour pressures within the experimental temperature interval.

The original vapour pressures reported in the literature and own results have to be treated with the same procedure. The primary vapour pressures available in the literature were treated using Eqs. (1) and (2) to evaluate the enthalpies of sublimation at 298.15 K, which are given in Table 3.

The sublimation enthalpies derived from the numerous and different methods (static, Knudsen effusion method, head space analysis, and transpiration) and uniformly adjusted to the reference temperature $T = 298.15 \text{ K}$ are in a good agreement within the evaluated experimental uncertainties, which are generally at the level of $\pm 1 \text{ kJ mol}^{-1}$ (see Table 3). The only somewhat outlying result is those from the HSA method. The reason for this is definitely the underdeveloped experimental techniques; however, the large uncertainty of $\pm 2.2 \text{ kJ mol}^{-1}$ brings this result somewhat in line with other available values. The uncertainties of the $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^o(298.15 \text{ K})$ -values were also re-assessed using

Table 3 Phenol: compilation of enthalpies of sublimation $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^o$ available in the literature

Method ^a	<i>T</i> -range K	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^o(T_{\text{av}})$ kJ mol ⁻¹	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^o(298.15 \text{ K})^{\text{b}}$ kJ mol ⁻¹	Refs.
n/a	270–313	68.1 ± 1.0	68.0 ± 1.1	28,29
K	283–303	68.2 ± 0.5	68.0 ± 0.9	28,30
S	273.2–308.2	68.1 ± 0.9	67.9 ± 1.0	31
T	278.3–310.6	69.5 ± 0.3	69.2 ± 0.6	31
S	278–305	67.6 ± 2.0	67.4 ± 2.1	32
K	230.4–273.2	69.6 ± 0.9	68.7 ± 0.5	33
HAS	263–298	65.3 ± 2.1	65.0 ± 2.2	34
n/a	282–313	68.7 ± 1.0	68.6 ± 1.1	35
n/a	273–313	68.8 ± 1.0	68.7 ± 1.1	35
T	277.2–302.9	68.8 ± 0.4	68.7 ± 0.7 ^c	36
			68.6 ± 0.3^d	Average

^aMethod: S=static; K=Knudsen effusion method; n/a=not available; HSA= head space analysis; T=transpiration

^bVapour pressures available in the literature were treated using Eqs. (1) and (2) to evaluate the enthalpies of sublimation at 298.15 K. Uncertainty of the sublimation enthalpy $u(\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^o)$ is the standard uncertainty (0.683 level of confidence, $k=1$) calculated according to a procedure described elsewhere [14, 15]. It includes uncertainties from the experimental conditions, uncertainties of vapour pressure, uncertainties from the fitting equation, and uncertainties from temperature adjustment to $T=298.15 \text{ K}$.

^cThe previously published primary vapour pressures data were recalculated in this work with the current heat capacity difference.

^dWeighted mean value. Value in bold was recommended for further thermochemical calculations.

the guidelines recommended in Ref. [14, 15]. Compilation of available sublimation enthalpies for phenol is given in Table 3. To obtain more reliance, all ten sublimation enthalpies $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^o$ of phenol were averaged by using uncertainty as the weighing factor. The weighted average value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^o(298.15 \text{ K}) = 68.6 \pm 0.3 \text{ kJ mol}^{-1}$ can be now used for calculation of the gas-phase enthalpy of formation according to Eq. 4. It should be also mentioned that this averaged sublimation is in agreement with those value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^o(298.15 \text{ K}) = 68.4 \pm 0.8 \text{ kJ mol}^{-1}$ derived from the Clarke–Glew equation [37] (see Table 2), proving consistency of the evaluated data.

Evaluation of vapour pressures over the liquid phenol and $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^o$ -values. Vapour pressure measurements over the liquid sample of phenol have been a popular endeavour since 1947 [31, 40–45]. The available vapour pressures are given in Fig. 1. It is obvious that vapour pressures are very consistent in the range close to the boiling temperature. The agreement in the temperature range near the melting point is rather poor. Equation (6) is also valid for the treatment of vapour pressure data measured over the liquid sample. In this case, all three adjustable parameters refer to the transition liquid–gas. The set of available experimental absolute vapour pressures over the liquid phenol is given in Table S2. We treated these data in the range from 332.4 to 455.1 K, and the coefficients of Eq. (6) are listed in Table 2. This time the experimental temperature range was sufficient for using the heat capacity difference as the adjustable parameter. However, the value $\Delta_{\text{l}}^{\text{g}}C_{p,m}^o = -70 + -7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ derived in Table 2 is subject to a significant uncertainty (due to some deviation of available vapour pressures in the range close to the melting point). In order to ascertain the required value, we derived the $\Delta_{\text{l}}^{\text{g}}C_{p,m}^o = -67.7 \pm 0.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ from approximation of the reliable experimental vapour pressures reported by Biddiscombe and Martin [31]. The latter value agrees with those calculated by Eq. (6), but it is more accurate, and it has been used to derive vaporisation enthalpies of phenol with the help of Eqs. (1) and (2), which are given in Table 4.

There are a total of six original papers on the vapour pressure temperatures dependences with the comprehensible primary information [31, 40–45]. In addition, there are six sets of Antoine's equation coefficients given in the Stephenson and Malanowski compilation [35], as well as a set of selected vapour pressures at different temperatures compiled by Stull [40]. The spread of vaporisation enthalpies derived from the static method and ebulliometry (and uniformly adjusted to the reference temperature $T = 298.15 \text{ K}$) is somewhat large compared to the sublimation enthalpies. However, the agreement among numerous data sets can be considered as sufficient if one takes into account that the experimental uncertainties assessed are generally below the

Table 4 Phenol: compilation of enthalpies of vaporisation $\Delta_1^g H_m^o$ available in the literature

Method ^a	T- range K	$\Delta_1^g H_m^o(T_{av})$ kJ mol ⁻¹	$\Delta_1^g H_m^o(298.15\text{ K})^b$ kJ mol ⁻¹	Refs.
n/a	313.3–455.1	55.2 ± 1.0	60.4 ± 1.1	40
S	414.3–454.3	48.6 ± 0.2	57.7 ± 0.9	41
E	380–455	50.0 ± 1.0	57.8 ± 1.2	42
E	306.9–454.9	51.7 ± 0.2	57.1 ± 0.5	43
E	343.7–454.9	55.2 ± 1.0	60.4 ± 1.1	44
S	394.3–455.3	49.0 ± 0.1	57.8 ± 0.8	31
n/a	455–655	44.9 ± 1.0	(62.3 ± 1.7)	35
n/a	314–395	55.0 ± 1.0	58.8 ± 1.1	35
n/a	387–456	49.5 ± 1.0	57.9 ± 1.2	35
n/a	449–526	45.6 ± 1.0	58.5 ± 1.5	35
n/a	520–625	43.8 ± 1.0	60.3 ± 1.8	35
n/a	383–473	49.1 ± 1.0	57.9 ± 1.3	35
E	363.1–390.9	53.6 ± 0.1	58.7 ± 0.6	45
			58.0 ± 0.3^c	Average

^aTechniques: E = ebulliometry; S = static; n/a = not available

^bVapour pressures available in the literature were treated using Eqs. (1) and (2) to evaluate the enthalpies of sublimation/vaporisation at 298.15 K. Uncertainty of the vaporisation enthalpy $u(\Delta_1^g H_m^o)$ is the standard uncertainty (0.683 level of confidence, $k=1$) calculated according to a procedure described elsewhere [14, 15]. It includes uncertainties from the experimental conditions, uncertainties of vapour pressure, uncertainties from the fitting equation, and uncertainties from temperature adjustment to $T=298.15\text{ K}$.

^cWeighted mean value. Value in parenthesis was excluded from the calculation of the mean. Value in bold was recommended for further thermochemical calculations.

level of $\pm 1.5\text{ kJ mol}^{-1}$ (see Table 4). We averaged twelve vaporisation enthalpies of phenol using uncertainty as a weighing factor. The weighted average value $\Delta_1^g H_m^o(298.15\text{ K}) = 58.0 \pm 0.3\text{ kJ mol}^{-1}$ can be now also used for calculation

$$\Delta_{cr}^1 H_m^o(298.15\text{ K}) / (\text{J mol}^{-1}) = \Delta_{cr}^1 H_m^o(T_{fus}/\text{K}) - \left(\Delta_{cr}^g C_{p,m}^o - \Delta_1^g C_{p,m}^o \right) \times [(T_{fus}/\text{K}) - 298.15\text{ K}] \quad (8)$$

of the gas-phase enthalpy of formation according to Eq. 4. The latter value is in very good agreement with those value $\Delta_1^g H_m^o(298.15\text{ K}) = 58.3 \pm 0.7\text{ kJ mol}^{-1}$ derived from the Clarke–Glew equation [37] (see Table 2), proving consistency of the evaluated data on vaporisation enthalpy.

The $\Delta_1^g H_m^o(298.15\text{ K})$ -values evaluated in Table 4 together with the $\Delta_{cr}^g H_m^o(298.15\text{ K})$ -values evaluated in Table 3 can be additionally used for a mutual validation of thermochemical data on phenol as follows.

Evaluation of $\Delta_{cr}^1 H_m^o$ -values. Vaporisation and sublimation enthalpies are related to the fusion enthalpy:

Table 5 Phenol: compilation of enthalpies of fusion $\Delta_{cr}^1 H_m^o$ available in the literature

T_{fus} K	$\Delta_{cr}^1 H_m^o(T_{fus})^a$ kJ mol ⁻¹	$\Delta_{cr}^1 H_m^o(298.15\text{ K})^b$ kJ mol ⁻¹	Ref
313.7	10.6 ± 1.0		46
314.1	12.1 ± 0.5		47
314.05	11.5 ± 0.1		48
314.0	11.5 ± 0.5		49
314.0	11.6 ± 0.2		36
314.05 ± 0.01 [48]	11.5 ± 0.1	10.8 ± 0.2^c	Average

^aUncertainty of the fusion enthalpy $U(\Delta_{cr}^1 H_m^o)$ is the expanded uncertainty (0.95 level of confidence, $k=2$)

^bAdjusted to the reference temperature according to Eq. (8).

^cWeighted mean value.

$$\Delta_{cr}^g H_m^o(298.15\text{ K}) = \Delta_1^g H_m^o(298.15\text{ K}) + \Delta_{cr}^1 H_m^o(298.15\text{ K}) \quad (9)$$

Consequently, using the evaluated fusion enthalpy we can establish the consistency or inconsistency of all three phase transitions: solid–liquid, solid–gas, and liquid gas. There are five original papers on fusion enthalpies of $\Delta_{cr}^1 H_m^o(T_{fus})$ [36, 46–49] (see Table 5). Uncertainties in the available results were not always reported. Therefore, the uncertainty intervals were assigned based on the uncertainties typical of each experimental method.

The available fusion enthalpies are in very close agreement (see Table 5). We averaged all five results for phenol using uncertainty as a weighing factor. The weighted average value $\Delta_{cr}^1 H_m^o(T_{fus}) = 11.5 \pm 0.1\text{ kJ mol}^{-1}$ has to be adjusted to the reference temperature $T=298.15\text{ K}$.

The adjustment of $\Delta_{cr}^1 H_m^o(T_{fus})$ to $T=298.15\text{ K}$ was performed with the help of the equation [38]:

With the $\Delta_{cr}^g C_{p,m}^o$ and $\Delta_1^g C_{p,m}^o$ values evaluated above. With this adjustment, the molar enthalpies of fusion, $\Delta_{cr}^1 H_m^o(298.15\text{ K})$, were calculated. Uncertainties in the temperature adjustment of fusion enthalpy from T_{fus} to the reference temperature were estimated to account with 30% to the total adjustment [50]. The adjusted value $\Delta_{cr}^1 H_m^o(298.15\text{ K}) = 10.8 \pm 0.5\text{ kJ mol}^{-1}$ can be now used for calculation of the “*theoretical*” sublimation enthalpy of phenol according to Eq. 7: $\Delta_{cr}^g H_m^o(298.15\text{ K}) = (58.04 \pm 0.25) + (10.8 \pm 0.2) = (68.8 \pm 0.3)\text{ kJ mol}^{-1}$ using values $\Delta_1^g H_m^o(298.15\text{ K})$ and $\Delta_{cr}^1 H_m^o(298.15\text{ K})$ evaluated in Table 4 and Table 5. This

“theoretical” sublimation enthalpy of phenol is in excellent agreement with the *experimental* weighted average value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K}) = (68.56 \pm 0.27)\text{ kJ}\cdot\text{mol}^{-1}$ evaluated in Table 3. Such an excellent agreement can be seen as the proof of the internal consistency of all three phase transitions: solid–liquid, solid–gas, and liquid–gas which were evaluated in this work.

Experiment and quantum chemistry: come together? The *experimental* weighted average value $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{cr}, 298.15\text{ K}) = -61.1 \pm 1.1\text{ kJ}\cdot\text{mol}^{-1}$ derived for phenol in Table 2 and the *experimental* weighted average value $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K}) = (68.5 \pm 0.5)\text{ kJ}\cdot\text{mol}^{-1}$ evaluated in Table 3 provides the *experimental* the gas-phase enthalpy of formation value $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g}, 298.15\text{ K})_{\text{exp}} = -92.5 \pm 1.2\text{ kJ}\cdot\text{mol}^{-1}$ according to Eq. 4. This *experimental* result for phenol is now in very good agreement with the *theoretical* value $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{G4}} = -90.8 \pm 3.5\text{ kJ}\cdot\text{mol}^{-1}$ calculated in this work by atomisation procedure, as well as with $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{G4}} = -91.8 \pm 2.5\text{ kJ}\cdot\text{mol}^{-1}$ calculated by Dorofeeva and Ryzhova [6] by using different isodesmic reactions.

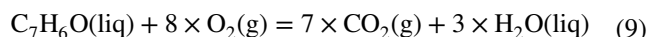
Thermochemistry of benzaldehyde

Evaluation of $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{liq})$ -values. We found five original papers dealing with the combustion experiments on benzaldehyde. The first data were reported by Stohmann et al. [51] in 1887. Taking into account the vintage of the result, we assigned the uncertainty interval of $\pm 4\text{ kJ}\cdot\text{mol}^{-1}$ to this value. Historically, the next data set was measured by Landrieu et al. [52]. The original paper was not available for us, but the combustion enthalpy (see Table 6) based only on two combustion experiments was compiled by Cox and Pilcher [4]. Lebedeva and Katin [53] also determined the enthalpy of combustion of benzaldehyde (see Table 6), which significantly differs from other available results. We

have recalculated enthalpy of formation of benzaldehyde using the combustion energies reported in that work. However, studying of the complete version of their paper shows no sources for the obvious systematic error.

Two sets of energies of combustion were determined by static-bomb calorimetry in National Physical laboratory of UK [54]. The first set was measured in this laboratory in 1963. The sample was purified by distillation but no quantitative estimate of purity made, except for an estimation of the benzoic acid content ($\geq 0.02\text{ mol per cent}$). The samples for combustion were enclosed in soda-glass ampoules, but combustion experiments are suffered from incompleteness of combustion. The recoveries of carbon dioxide ranged from 99.96 to 100.02 per cent of the theoretical; the results have been calculated only on the basis of masses derived from the yields of carbon dioxide. The second series was repeated in 1974 in this laboratory. Whilst the 1963 work lacked a quantitative determination of sample purity and the 1974 work also suffered from difficulties in obtaining absolutely clean combustions, the results of the two series do not differ significantly. Since different samples and different calorimeters were employed, this is good evidence that the values obtained were, in fact, reliable.

The standard molar enthalpies of formation $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{liq})$ of benzaldehyde were derived from the standard molar enthalpies of combustion $\Delta H_{\text{m}}^{\circ}(\text{liq})$ evaluated for every literature source (see Table 6). Combustion results were referenced to the reaction:



The $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{liq})$ -values of benzaldehyde were obtained applying the Hess’s law to Eq. (9). In order to get more confidence, four $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{liq})$ -values were averaged by using uncertainty as the weighing factor. The weighted average value $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{liq}, 298.15\text{ K}) = -87.8 \pm 1.9\text{ kJ}\cdot\text{mol}^{-1}$ can be

Table 6 Benzaldehyde: compilation of enthalpies of formation $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{liq})$ available in the literature ($\text{kJ}\cdot\text{mol}^{-1}$)

Compound	$\Delta_{\text{c}}H_{\text{m}}^{\circ}(\text{l})$	$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{l})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}$ ^a	$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{exp}}$	$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{G4}}$ ^b
1		2	3	4	5
Benzaldehyde(liq)	-3522.0 ± 3.9 [3, 51]	-90.1 ± 4.0			
	-3525.9 ± 14 [4, 52]	-86.2 ± 14			
	(-3531.2 ± 2.1) [53]	(-80.9 ± 2.3)			
	-3524.4 ± 3.6 [54–1963]	-87.7 ± 3.7			
	-3525.2 ± 2.5 [54–1974]	-86.9 ± 2.7			
		-87.8 ± 1.9 ^c	49.4 ± 0.4	-38.4 ± 1.9	-38.7 ± 3.5

^aEvaluated vaporisation enthalpy from Table 7

^bTheoretical enthalpies of formation calculated using the G4 method according to atomisation procedure

^cWeighted mean value. Value in parenthesis was excluded from the calculation of the mean. Value in bold was recommended for further thermochemical calculations

Uncertainties in this table are the expanded uncertainty (0.95 level of confidence, $k=2$)

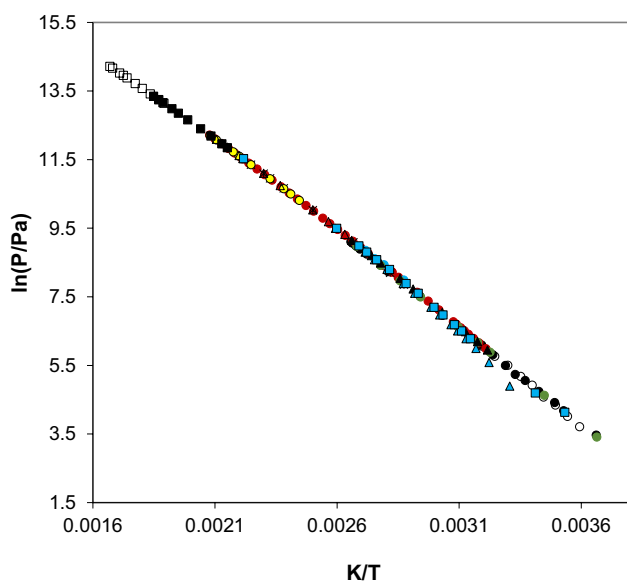


Fig. 2 Temperature dependence of vapour pressures for the benzaldehyde: ○—transpiration [61]; ●—static [57]; red round—ebulliometry [54]; blue round—ebulliometry [59]; blue triangle—ref. [55]; black cross—ref. [35-I]; green round—ref. [35-II]; yellow round—ref. [35-III]; ▲—ref. [35-IV]; △—ref. [35-V]; ■—ref. [35-VI]; □—ref. [35-VII]. Data from ref. [58] are not presented on this plot

Table 7 Thermodynamic functions of vaporisation of benzaldehyde ($T=298.15$ K)

T -range K	$\Delta_1^{\text{g}}G_{\text{m}}^{\circ}$ kJ mol $^{-1}$	$\Delta_1^{\text{g}}H_{\text{m}}^{\circ}$ kJ mol $^{-1}$	$-\Delta_1^{\text{g}}C_{\text{p,m}}^{\circ}$ J·mol $^{-1}$ ·K $^{-1}$
278.4–481.4	15.80 ± 0.01	49.1 ± 0.2	38 ± 5

Uncertainties in this table are the standard uncertainty (0.683 level of confidence, $k=1$)

now used for calculation of the gas-phase enthalpy of formation according to Eq. (4).

Evaluation of vapour pressures over the liquid benzaldehyde and $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}$ -values. The first vapour pressure measurements on benzaldehyde were reported by Kahlbaum [55] and von Rechenberg [56]. These sources are not easily available, but fortunately the primary vapour pressures were listed in paper by de Mare et al. [57]. The available experimental absolute vapour pressures are given in Fig. 2. The numerical values of experimental absolute vapour pressures over the liquid benzaldehyde are given in Table S3. It has turned out that the available vapour pressures on benzaldehyde are remarkably consistent (except for few data points measured by Kahlbaum [55] at low temperatures). We treated these data in the range from 278.4 to 481.4 K, and the coefficients of Eq. (6) are listed in Table 7.

The value $\Delta_1^{\text{g}}C_{\text{p,m}}^{\circ} = -38 \pm 5$ J·mol $^{-1}$ ·K $^{-1}$ calculated in Table 7 is in acceptable agreement with the value

Table 8 Benzaldehyde: compilation of enthalpies of vaporisation $\Delta_1^{\text{g}}H_{\text{m}}^{\circ}$ available in the literature

Method ^a	T -range	$\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(T_{\text{av}})$	$\Delta_1^{\text{g}}H_{\text{m}}^{\circ}$	Refs.
	K	kJ mol $^{-1}$	(298.15 K) ^b kJ mol $^{-1}$	
n/a	315.7–451.5	48.5 ± 1.5	51.9 ± 1.6	55
n/a	283.2–451.2	47.7 ± 0.3	50.2 ± 0.5	56
n/a	299.4–452.2	48.8 ± 0.8	52.0 ± 0.9	40
S	452.2–621.2	41.8 ± 1.2	53.0 ± 1.6	58
S			49.8 ± 0.8	53
S	273.2–376.5	47.0 ± 0.2	48.3 ± 0.3	57
E	311.6–481.4	45.8 ± 0.1	49.8 ± 0.5	54
E	348.2–368.2	45.4 ± 1.5	48.2 ± 1.6	59
n/a	348–452	45.8 ± 1.0	50.7 ± 1.1	35-I
n/a	273–373	46.8 ± 1.0	48.0 ± 1.1	35-II
n/a	409–481	43.0 ± 1.0	49.9 ± 1.2	35-III
n/a	311–376	47.7 ± 1.0	49.9 ± 1.1	35-IV
n/a	370–475	43.8 ± 1.0	49.7 ± 1.2	35-V
n/a	465–541	41.3 ± 2.0	51.0 ± 2.2	35-VI
n/a	529–599	40.4 ± 2.0	53.0 ± 2.4	35-VI
CGC			49.1 ± 2.1	60
T	278.4–313.2	49.1 ± 0.6	$48.9 \pm 0.7^{\text{c}}$	61
			$49.4 \pm 0.2^{\text{d}}$	Average

^aTechniques: E=ebulliometry; T=transpiration; S=static; n/a=not available; CGC=correlation gas-chromatography

^bVapour pressures available in the literature were treated using Eqs. (1) and (2) to evaluate the enthalpies of vaporisation at 298.15 K. Uncertainty of the vaporisation enthalpy $u(\Delta_1^{\text{g}}H_{\text{m}}^{\circ})$ is the standard uncertainty (0.683 level of confidence, $k=1$) calculated according to a procedure described elsewhere [14, 15]. It includes uncertainties from the experimental conditions, uncertainties of vapour pressure, uncertainties from the fitting equation, and uncertainties from temperature adjustment to $T=298.15$ K.

^cThe previously published primary vapour pressures data were recalculated in this work with the current heat capacity difference.

^dWeighted mean value. Value in parenthesis was excluded from the calculation of the mean. Value in bold is recommended for further thermochemical calculations.

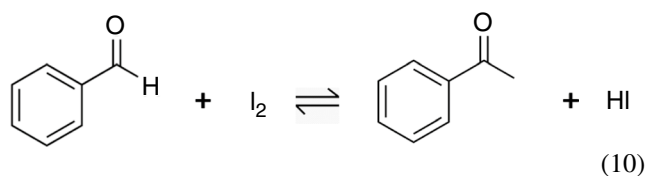
$\Delta_1^{\text{g}}C_{\text{p,m}}^{\circ} = -47.4 \pm 0.5$ J·mol $^{-1}$ ·K $^{-1}$ derived from approximation of the reliable experimental vapour pressures reported by Ambrose et al. [54]. The latter value is more accurate, and it has been used to derive vaporisation enthalpies of benzaldehyde with the help of Eqs. (1) and (2). The results of these calculations are given in Table 8.

Surprisingly, even the old results reported by Kahlbaum [55] and von Rechenberg [56] are in good agreement with all other contemporary data (see Table 8). We collected seven original data sets (see Table S3) on temperature vapour pressure dependences with traceable primary data. Additionally, we used seven sets of Antoine's equation coefficients compiled by Stephenson and Malanowski [35],

as well as the smoothed vapour pressures and different temperatures selected in compilation by Stull [40]. We averaged seventeen vaporisation enthalpies of benzaldehyde using uncertainty as a weighing factor. The weighted average value $\Delta_1^g H_m^o(298.15 \text{ K}) = 49.37 \pm 0.18 \text{ kJ mol}^{-1}$ can be now also used for calculation of the gas-phase enthalpy of formation according to Eq. (4). This result is in very good agreement with those value $\Delta_1^g H_m^o(298.15 \text{ K}) = 49.1 \pm 0.2 \text{ kJ mol}^{-1}$ derived from the Clarke–Glew equation [37] (see Table 7), giving an additional proof of the consistency of the evaluated data on the vaporisation enthalpy of benzaldehyde.

Comparison of experimental and quantum chemical results for benzaldehydes. The *experimental* weighted average value $\Delta_f H_m^o(\text{liq}, 298.15 \text{ K}) = -87.8 \pm 1.9 \text{ kJ mol}^{-1}$ derived for benzaldehyde in Table 6 and the *experimental* weighted average value $\Delta_1^g H_m^o(298.15 \text{ K}) = (49.4 \pm 0.4) \text{ kJ mol}^{-1}$ evaluated in Table 8 give the *experimental* the gas-phase enthalpy of formation value $\Delta_f H_m^o(\text{g}, 298.15 \text{ K})_{\text{exp}} = -38.3 \pm 1.2 \text{ kJ mol}^{-1}$ according to Eq. (4). This *experimental* result for benzaldehyde is in very good agreement with the *theoretical* value $\Delta_f H_m^o(\text{g})_{\text{G4}} = -38.7 \pm 3.5 \text{ kJ mol}^{-1}$ calculated in this work with the high-level quantum chemical method G4.

Validation of gas-phase enthalpy of formation of benzaldehydes. Solly and Benson [62] studied the equilibrium of the reaction of benzaldehyde with iodine:



The enthalpy of the gas phase reaction according to Eq. (10) $\Delta_r H_m^o(\text{g}) = 12.6 \pm 4.2 \text{ kJ mol}^{-1}$ was derived. The standard molar enthalpies of formation of the reaction (Eq. 10) participants are available in the literature: $\Delta_f H_m^o(\text{g}, 298.15 \text{ K}) = 62.4 \pm 0.1 \text{ kJ mol}^{-1}$ [63] for iodine, $\Delta_f H_m^o(\text{g}, 298.15 \text{ K}) = 26.5 \pm 0.1 \text{ kJ mol}^{-1}$ [63] for HI, and $\Delta_f H_m^o(\text{g}, 298.15 \text{ K}) = 10.5 \pm 1.8 \text{ kJ mol}^{-1}$ [64] for benzoyl iodide. The *experimental* gas-phase enthalpy of formation value $\Delta_f H_m^o(\text{g}, 298.15 \text{ K})_{\text{exp}} = -38.0 \pm 4.6 \text{ kJ mol}^{-1}$ was calculated according to the Hess's law applied to Eq. (10). This *experimental* result for benzaldehyde is in very good agreement with the experimental result derived from combination of combustion calorimetry results (see Table 6) with evaluated vaporisation enthalpy $\Delta_f H_m^o(\text{g}, 298.15 \text{ K})_{\text{exp}} = -38.4 \pm 1.9 \text{ kJ mol}^{-1}$ (see Table 8), as well as with the *theoretical* value $\Delta_f H_m^o(\text{g})_{\text{G4}} = -38.7 \pm 3.5 \text{ kJ mol}^{-1}$ calculated in this work with the high-level quantum chemical method G4. Such a very good agreement can be taken as evidence of the internal consistency of experimental and *theoretical* results evaluated in this work for benzaldehyde.

Thermochemistry of anisole

Evaluation of $\Delta_f H_m^o(\text{liq})$ -values. Four original papers dealing with the combustion experiments on anisole were found in the literature [5, 23, 53, 64]. Badoche [23] reported four combustion experiments performed at 290.15 K. We have recalculated the primary results with current thermochemical quantities and adjusted the combustion enthalpy to the reference temperature $T = 298.15 \text{ K}$ (see Table 9).

Lebedeva and Katin [53] reported the energy of combustion of anisole (see Table 9). We have recalculated (see Table 9) enthalpy of formation of anisole using the combustion energies reported in that work. Fenwick et al. [64] from the National Physical Laboratory of UK also reported the enthalpy of combustion of anisole (see Table 9). We have recalculated the enthalpy of formation of anisole using the combustion energies reported in that work and current thermochemical quantities (see Table 6). The most recent combustion experiments on anisole were performed at the University of Lisbon with the isoperibol static-bomb combustion calorimeter [5]. The anisole sample was burned inside a polyethylene ampule. All four results on combustion enthalpies are in agreement within their experimental uncertainties.

The standard molar enthalpies of formation $\Delta_f H_m^o(\text{liq})$ of anisole were derived from the standard molar enthalpies of combustion $\Delta H_m^o(\text{liq})$ evaluated for every literature source (see Table 9). Combustion results were referenced to the reaction:

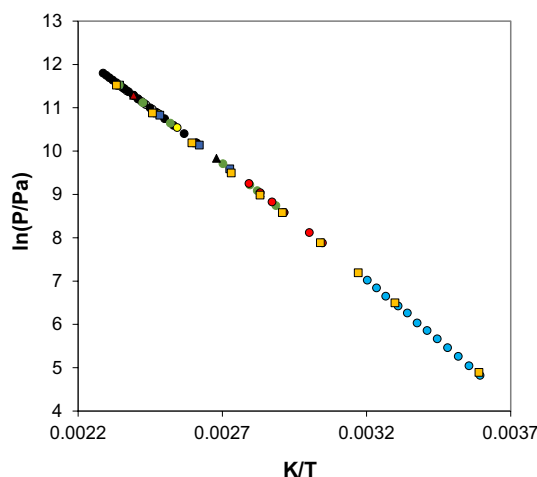
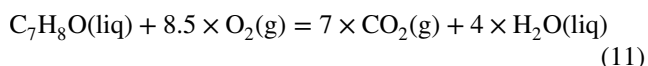


Fig. 3 Temperature dependence of vapour pressures for the anisole: blue round—transpiration [73]; ●—ebulliometry [66]; ○—ebulliometry [65]; red triangle—ebulliometry [74]; purple square—calorimetry [67]; ▲—ebulliometry [70]; green round—ref. [42]; yellow round—ebulliometry [71]; red round—ebulliometry [69]; yellow square—ref. [40]. Data from ref. [58] are not presented on this plot

Table 9 Anisole: compilation of enthalpies of formation $\Delta_f H_m^\circ$ (liq) available in the literature (kJ mol^{-1})

Compound	$\Delta_c H_m^\circ(\text{l})$	$\Delta_f H_m^\circ(\text{l})$	$\Delta_1^g H_m^\circ$ ^a	$\Delta_f H_m^\circ(\text{g})_{\text{exp}}$	$\Delta_f H_m^\circ(\text{g})_{\text{G4}}$ ^b
Anisole (liq)	-3781.4 ± 1.7 [23]	-116.5 ± 1.9			
	-3779.7 ± 1.0 [53]	-118.2 ± 1.3			
	-3783.0 ± 1.1 [64]	-114.9 ± 1.5			
	-3780.8 ± 1.1 [5]	-117.1 ± 1.4			
		-116.9 ± 0.7	46.6 ± 0.2	-70.3 ± 0.7	-71.3 ± 3.5

^aEvaluated vaporisation enthalpy from Table 11^bTheoretical enthalpies of formation calculated using the G4 method according to atomisation procedure
Uncertainties in this table are the expanded uncertainty (0.95 level of confidence, $k=2$)

The $\Delta_f H_m^\circ(\text{liq})$ -values of anisole were obtained (see Table 11) applying the Hess's law to Eq. (11). To get more trust, four $\Delta_f H_m^\circ(\text{liq})$ -values were averaged by using uncertainty as the weighing factor. The weighted average value $\Delta_f H_m^\circ(\text{liq}, 298.15 \text{ K}) = -116.9 \pm 0.7 \text{ kJ mol}^{-1}$ can be now used for calculation of the gas-phase enthalpy of formation according to Eq. (4).

Evaluation of vapour pressures over the liquid anisole and $\Delta_1^g H_m^\circ$ -values. The vapour pressures of anisole measured with different methods at different temperatures are very consistent, as can be seen from Fig. 3. The primary vapour pressure data [40, 42, 58, 64–74] are collected in Table S4. We approximated them using the Clark–Glue equation, in order to derive thermodynamics functions of vaporisation (see Table 10). The value of $\Delta_1^g C_{p,m}^\circ = -47.4 \pm 0.7 \text{ J mol}^{-1} \cdot \text{K}^{-1}$ derived in Table 10 was used to derive individual vaporisation enthalpies of anisole according to Eq. 2 from vapour pressure temperature dependences. Results of these calculations are compiled in Table 11.

Compared to phenol and benzaldehyde, the vaporisation thermodynamics of anisole was investigated not only by the indirect methods (from vapour pressure temperature dependence) [40, 42, 58, 64–74], but also directly using the vaporisation calorimetry [5, 64, 67, 68]. It has turned

Table 10 Thermodynamic functions of vaporisation of anisole ($T=298.15 \text{ K}$)

T -range K	$\Delta_1^g G_m^\circ$ kJ mol^{-1}	$\Delta_1^g H_m^\circ$ kJ mol^{-1}	$-\Delta_1^g C_{p,m}^\circ$ $\text{J mol}^{-1} \cdot \text{K}^{-1}$
278.3–437.3	13.2 ± 0.1	46.6 ± 0.1	46.7 ± 1.0

Uncertainties in this table are the standard uncertainty (0.683 level of confidence, $k=1$)

out that the direct and indirect values of $\Delta_1^g H_m^\circ$ (298.15 K)-values agree within their experimental uncertainties. We averaged sixteen vaporisation enthalpies of anisole using uncertainty as a weighing factor. The weighted average value $\Delta_1^g H_m^\circ(298.15 \text{ K}) = 46.6 \pm 0.1 \text{ kJ mol}^{-1}$ is indistinguishable from the result from Clark–Glue equation (see Table 10). It can be used for the calculation of the gas-phase enthalpy of formation of anisole according to Eq. 4.

Comparison of experiment and quantum chemical results for anisole. The experimental weighted average value $\Delta_f H_m^\circ(\text{liq}, 298.15 \text{ K}) = -116.9 \pm 0.7 \text{ kJ mol}^{-1}$ derived for anisole in Table 9 and the experimental weighted average value $\Delta_f H_m^\circ(298.15 \text{ K}) = (46.6 \pm 0.2) \text{ kJ mol}^{-1}$ evaluated in Table 11 give the experimental the gas-phase enthalpy of formation value $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})_{\text{exp}} = -70.3 \pm 0.7 \text{ kJ mol}^{-1}$ according to Eq. 4. This experimental result for anisole is in very good agreement with the theoretical value $\Delta_f H_m^\circ(\text{g})_{\text{G4}} = -71.3 \pm 3.5 \text{ kJ mol}^{-1}$ calculated in this work with the high-level quantum chemical method G4, as well as with the theoretical value $\Delta_f H_m^\circ(\text{g})_{\text{theor}} = -70.8 \pm 3.2 \text{ kJ mol}^{-1}$ [5] calculated with significantly more sophisticated W2-F12 method.

Conclusions

The consistent sets of standard molar thermodynamic properties of formation and phase transitions for phenol, benzaldehyde, and anisole were evaluated in this work. The data on the resulting experimental gas-phase enthalpies of formation were in close agreement with the theoretical values calculated using the high-level quantum-chemical methods. Thermodynamic properties for these benzene derivatives, which model lignin structural units, were recommended as reliable benchmark properties for thermochemical calculations of the energetics of the lignin valorisation technologies.

Table 11 Anisole: compilation of enthalpies of vaporisation $\Delta_1^{\text{g}}H_m^{\text{o}}$ available in the literature

Method ^a	T- range K	$\Delta_1^{\text{g}}H_m^{\text{o}}(T_{\text{av}})$ kJ mol ⁻¹	$\Delta_1^{\text{g}}H_m^{\text{o}}(298.15 \text{ K})^{\text{b}}$ kJ mol ⁻¹	Refs.
n/a	278.6–428.7	43.7 ± 1.0	45.8 ± 1.1	40
E	346.5–426.9	42.5 ± 0.1	46.5 ± 0.4	42
E	427–639	39.5 ± 0.4	(49.9 ± 1.0)	58
E	405.0–426.4	40.3 ± 0.2	45.7 ± 0.8	65
E	383.0–437.3	41.4 ± 0.1	46.6 ± 0.5	66
C	366.9–426.7		46.8 ± 0.2 ^c	67
C	366.9–426.7	42.1 ± 0.1	46.5 ± 0.5 ^d	67
S			(38.2 ± 0.4)	53
C	298.15		46.8 ± 0.2	64
C			46.9 ± 0.5	68
E	328.2–358.2	44.8 ± 0.3	46.8 ± 0.5 ^e	69
E	314–427	43.8 ± 0.3	46.9 ± 0.4 ^f	69
E	353–373	43.8 ± 1.0	46.8 ± 1.2	70
E	393.2–403.2	41.7 ± 1.0	46.3 ± 1.7	71
CGC			45.3 ± 2.0	60
CGC			(44.3 ± 2.0)	72
T	278.3–312.3	46.5 ± 0.2	46.3 ± 0.3 ^g	73
E	383.1–426.5	41.8 ± 0.1	46.6 ± 0.5	74
CDMC	298.15		46.4 ± 0.3	5
			46.6 ± 0.1^h	Average

^aTechniques: E=ebullimetry; T=transpiration; S=static; n/a=not available; CGC=correlation gas chromatography; C=calorimetry; CDMC=Calvet-drop microcalorimetry

^bVapour pressures available in the literature were treated using Eqs. (1) and (2) to evaluate the enthalpies of vaporisation at 298.15 K. Uncertainty of the vaporisation enthalpy $u(\Delta_1^{\text{g}}H_m^{\text{o}})$ is the standard uncertainty (0.683 level of confidence, $k=1$) calculated according to a procedure described elsewhere [14, 15]. It includes uncertainties from the experimental conditions, uncertainties of vapour pressure, uncertainties from the fitting equation, and uncertainties from temperature adjustment to $T=298.15 \text{ K}$.

^cDerived by extrapolation of calorimetric results measured at elevated temperatures to the $T=298.15 \text{ K}$

^dDerived from vapour pressures temperature dependence

^eDerived from studies of binary mixtures

^fDerived from study of pure anisole

^gThe previously published primary vapour pressures data were recalculated in this work with the current heat capacity difference.

^hWeighted mean value. Values in parenthesis were excluded from the calculation of the mean. Value in bold was recommended for further thermochemical calculations.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10973-021-10924-x>.

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