



Benchmark thermodynamic properties of 1,3-propanediol: Comprehensive experimental and theoretical study



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ABSTRACT

Thermochemical properties of 1,3-propanediol are in disarray. A new standard ($p^\circ = 0.1$ MPa) molar enthalpy of formation at the temperature $T = 298.15$ K of the liquid 1,3-propanediol was measured using combustion calorimetry. A new molar enthalpy of vaporisation of 1,3-propanediol was derived from the vapour pressure temperature dependence measured by the transpiration method. Thermodynamic data on 1,3-propanediol available in the literature were collected, evaluated, and combined with own experimental results. This collection together with the new experimental results reported here has helped to resolve contradictions in the available enthalpies of formation data and to recommend the set of vaporisation and formation enthalpies for 1,3-propanediol at $T = 298.15$ K (in $\text{kJ} \cdot \text{mol}^{-1}$): $\Delta_f H_m^\circ(\text{g}) = -(410.6 \pm 2.2)$, $\Delta_f H_m^\circ(\text{l}) = -(481.8 \pm 2.2)$, and $\Delta_v H_m^\circ = (71.2 \pm 0.2)$ as the reliable benchmark properties for further thermochemical calculations. Quantum-chemical calculations of the gas phase molar enthalpy of formation of 1,3-propanediol have been performed using the G3MP2 method and results were in excellent agreement with the recommended experimental values. The standard molar entropy of formation and the standard molar Gibbs function of formation have been calculated.

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1. Introduction

The manufacturing of renewably-sourced platform chemicals and polymers is an active area of interest [1]. Large scale fermentation of glycerol [2] or glucose [3] to form 1,3-propanediol is an attractive way for valorisation of renewable feed stocks since 1,3-propanediol is a valuable precursor for production high value polymers and intermediates [3]. New strategies to utilise renewable feedstock into value-added products are important for the future competitiveness of the chemical industry. Chemical feasibility of new strategies has to be assessed using thermodynamic calculations. Reliability of the prediction is crucially dependent on the quality of experimental data involved in the calculations. Surprisingly, the available thermochemical values for alkanediols are in disarray [4]. The standard molar enthalpy of formation, $\Delta_f H_m^\circ$, of 1,3-propanediol in the liquid state reported in the literature [5–7] from combustion calorimetry measurements show spread over $15 \text{ kJ} \cdot \text{mol}^{-1}$. New additional experiments with 1,3-propanediol

are intending to resolve contradictions among available data. This contribution complements and extends our previous work on thermodynamics of aliphatic diols by our group [4,8,9]. The aim of this study is an experimental and computational study of 1,3-propanediol in order to evaluate available thermochemical properties.

2. Materials and methods

2.1. Materials

A sample of 1,3-propanediol available from Alfa Aesar with mass fraction purity 0.99 was further purified by fractional distillation with a spinning-band column in vacuum. No impurities (greater than 0.02 mass percent) could be detected in the samples used for the combustion experiments and the vapour pressure measurements. The degree of purity was determined using a GC with capillary column HP-5 was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm . The standard temperature program of the GC was $T = 333$ K for 180 s followed by a heating rate of $0.167 \text{ K} \cdot \text{s}^{-1}$ to $T = 523$ K. Provenance and purity of the compound prepared for thermochemical studies in this work are given in [table S1 \(Supplementary information\)](#).

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2.2. Vapour pressure measurements. Transpiration method

Vapour pressures of 1,3-propanediol were determined using the method of transpiration [10] in a saturated nitrogen stream. About 0.5 g of the sample was mixed with small glass beads and placed in a thermostatted U-shaped saturator. A well defined nitrogen stream was passed through the saturator at a constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample of 1,3-propanediol was determined by GC analysis using an external standard n -C₉H₂₀. The absolute vapour pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance i , values of p_i were calculated with equation:

$$P_i = m_i \cdot R \cdot T_a / V \cdot M_i; \quad V = V_{N_2} + V_i; \quad (V_{N_2} \gg V_i), \quad (1)$$

where $R = 8.314462 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i its volume contribution to the gaseous phase. V_{N_2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N_2} was determined from the flow rate and the time measurement. Experimental results are given in tables 1 and 2.

the 10 mL pycnometer using the syringe of 250 μL nominal volume and the mixture was analysed by GC with the same reproducibility.

- The volume of the carrier gas V_{N_2} . For the transpiration experiments with duration over few hours the value of V_{N_2} was directly measured by Honeywell S&C – HAFBLF0200-C2AX5 digital flow rate sensor with uncertainty at the level of 2.5%. For the shorter experiments, the carrier gas flow rate was measured with the HP Agilent soap film flow meter (-model 0101-0113). The value of V_{N_2} was calculated from the gas-flow and time measurements with uncertainty of 1%.
- The temperature of saturator was kept constant within (± 0.2 K) using a circulating thermostat. The temperature was measured using a calibrated Pt-100 thermometer with resolution of $T = 0.2$ K.
- The ambient temperature T_a of the volume V_{N_2} measurements was measured using the calibrated Pt-100 with uncertainty ± 0.2 K.
- The atmospheric pressure was measured using a digital pressure indicator with uncertainty ± 2 hPa absolute.

Uncertainties resulting from correlations are reported as standard deviations (u). Uncertainties associated with combined results were evaluated as follows:

$u(p)/p =$	
$(0.0001/0.05) = 0.0040 \cdot 100 = 0.20\%$	mass of the reference sample
$(0.0001/0.03) = 0.0067 \cdot 100 = 0.67\%$	mass of the sample under study
$(0.01/5) + (0.01/10) = 0.0030 \cdot 100 = 0.30\%$	volumes of calibrated pycnometers
$(0.25/200) + (0.1/100) = 0.0022 \cdot 100 = 0.22\%$	volume of the standard solution
$(0.02/2) + (0.02/2) = 0.02 \cdot 100 = 2.0\%$	GC injections(calibration + determination)
$(0.01/2) = 0.005 \cdot 100 = 0.5\%$	volume of transporting gas
$(0.2/323) + (0.2/298) = 0.00129 \cdot 100 = 0.13\%$	T – measurements(saturator + ambient)
$(2/1000) = 0.002 \cdot 100 = 0.20\%$	ambient atmospheric pressure
$u(p)/p = (u_1^2 + u_2^2 + \dots)^{0.5} \cdot 100 = 2.1\%$	combined uncertainties.

2.3. Uncertainties of vapour pressure measurements

The experimental quantities measured to obtain the vapour pressures and enthalpies of vaporisation are as follows:

- The mass, m_i , of compound collected in the cold trap. This amount was determined by GC analysis using an external standard. This GC procedure consists of two steps: calibration of the FID using two reference solutions and injecting of the mixture of the transported sample with the well-defined amount of the standard solution. For the first step, about 0.03 g of sample was weighed in 5 mL calibrated pycnometer, and about 0.05 g of the standard compound (hydrocarbon n -C_nH_{2n+2}) was weighed in 10 mL calibrated pycnometer. We used KERN ACJ 220-4 m balances with the resolution of ± 0.0001 g. Both pycnometers were filled with acetonitrile with uncertainty ± 0.01 mL. Mixtures for the FID calibration were prepared using the Hamilton syringes of the Gastight 1700 series with (100 and 250) μL volume. Calibration mixtures were analysed by GC with the repeatability within (1 to 2)%. For the mass determination the cold trap was charged with 200 μL of the standard solution from

It has turned out that accuracy of vapour pressures measured by transpiration method governed mostly by the reproducibility of the GC analysis as well as by the volume V_{N_2} determination.

The standard uncertainties (u) of the measured vapour pressures have been calculated to be:

$$u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa}) \text{ for } p > 5 \text{ to } 1000 \text{ Pa,}$$

$$u(p/\text{Pa}) = 0.005 + 0.025(p/\text{Pa}) \text{ for } p < 5 \text{ Pa.}$$

To validate system operation, the vapour pressure of naphthalene was determined at $p = (1 \text{ to } 500) \text{ Pa}$ experimental vapour pressure of naphthalene obtained using this procedure agreed with the results reported in the literature [11] to within (0.6 to 2.5)%. For validation of our uncertainty estimations we measured vapour pressures for series of n -alkanols [10] where reliable values at $p = (0.1 \text{ to } 1000) \text{ Pa}$ from different methods were available. It has turned out that vapour pressures of n -alkanols derived from the transpiration method were comparable with available high-precision results generally within (1 to 3)% in agreement with our estimations.

TABLE 1

Absolute vapour pressures p , vaporisation enthalpies $\Delta_f^g H_m^\circ$, and vaporisation entropies $\Delta_f^g S_m^\circ$ obtained by the transpiration method.

T/K^a	m/mg^b	$V(\text{N}_2)/\text{dm}^3$	T_a/K^d	Flow/ $\text{dm}^3 \cdot \text{h}^{-1}$	p/Pa^e	$u(p)/\text{Pa}$	$\Delta_f^g H_m^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f^g S_m^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
1,3-propanediol; $\Delta_f^g H_m^\circ (T = 298.15 \text{ K}) = (70.5 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p/\text{Pa}) = \frac{301.7}{R} - \frac{87374.0}{R(T/K)} - \frac{56.5}{R} \ln\left(\frac{T/K}{298.15}\right)$								
292.5	1.86	36.12	295.8	3.01	1.67	0.05	70.85	150.8
293.5 ^f	2.11	37.05	297.9	2.94	1.86	0.05	70.79	150.7
296.4	1.87	25.33	295.8	3.01	2.39	0.06	70.63	149.8
300.4	2.05	19.21	295.8	3.01	3.46	0.09	70.40	149.0
303.2 ^f	1.39	10.12	297.9	2.90	4.47	0.12	70.25	148.4
306.3	2.13	11.79	295.8	3.01	5.84	0.17	70.07	147.8
309.3 ^f	0.94	3.87	297.9	2.90	7.88	0.22	69.90	147.5
312.2 ^f	1.88	6.15	297.9	2.90	9.97	0.27	69.74	146.8
315.3 ^f	2.22	5.43	297.9	2.99	13.29	0.36	69.56	146.4
318.4 ^f	2.32	4.56	297.9	2.99	16.59	0.44	69.39	145.6
321.3 ^f	2.32	3.49	297.9	2.99	21.68	0.57	69.22	145.3
324.3 ^f	2.41	2.84	297.9	2.99	27.64	0.72	69.05	144.8
327.3 ^f	2.29	2.09	297.9	2.99	35.58	0.91	68.88	144.5
330.3 ^f	2.07	1.54	297.9	2.99	43.72	1.12	68.71	143.8
333.5 ^f	2.04	1.19	297.9	2.99	55.56	1.41	68.53	143.2
336.4 ^f	1.93	0.920	297.9	2.99	68.42	1.73	68.37	142.7
338.7	5.58	2.22	295.8	1.33	81.45	2.06	68.24	142.4
339.4 ^f	2.07	0.798	297.9	2.99	84.64	2.14	68.20	142.2
342.3 ^f	1.93	0.598	297.9	2.99	105.3	2.7	68.04	141.8
344.3	5.22	1.40	295.8	1.33	120.8	3.1	67.92	141.4
346.4	5.24	1.22	295.8	1.33	139.0	3.5	67.81	141.1

^a Saturation temperature ($u(T) = 0.1 \text{ K}$).^b Mass of transferred sample condensed at $T = 243 \text{ K}$.^c Volume of nitrogen ($u(V) = 0.005 \text{ dm}^3$) used to transfer m ($u(m) = 0.0001 \text{ g}$) of the sample.^d T_a is the temperature of the soap bubble meter used for measurement of the gas flow.^e Vapour pressure at temperature T , calculated from the m and the residual vapour pressure at $T = 243 \text{ K}$.^f Experimental results from our previous transpiration study [4].

2.4. Combustion calorimetry

The molar enthalpy of combustion of 1,3-propanediol was measured with an isoperibolic calorimeter with a static bomb and a stirred water bath. The liquid sample was placed (under an inert atmosphere in a glove-box) in a polythene ampoule (Fa. NeoLab, Heidelberg, Germany). The sample was transferred into the polyethylene bulb with a syringe under nitrogen stream in a glove-box. The fine neck of the container was compressed with a special tweezers and was sealed outside the glove-box by heating of the neck in a close proximity to a glowing wire. Then, the container was placed in the crucible and was burned in oxygen at a pressure 3.04 MPa. The detailed procedure has been described previously [12]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter $\varepsilon_{\text{calor}} = (14875.04 \pm 0.95) \text{ J} \cdot \text{K}^{-1}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). For the reduction of the data to standard conditions, conventional procedures [8] were used. Auxiliary data are collected in table S2. Correction for nitric acid formation was based on titration with $0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ NaOH}$ (aq). The residual water content 971.4 ppm in the sample was determined by Karl Fischer titration before starting experiments and appropriate corrections have been made for combustion results. Results for combustion experiments are summarised in table 3.

3. Results and discussion

3.1. Vapour pressures of 1,3-propanediol

Temperature dependence of vapour pressures p_i measured for 1,3-propanediol was fitted with the following equation [10]:

$$R \cdot \ln p_i = a + \frac{b}{T} + \Delta_f^g C_{p,m}^\circ \cdot \ln\left(\frac{T}{T_0}\right), \quad (2)$$

where a and b are adjustable parameters and $\Delta_f^g C_{p,m}^\circ$ is the difference of the molar heat capacities of the gaseous and the liquid phase respectively. T_0 appearing in equation (2) is an arbitrarily chosen reference temperature (which has been chosen to be $T = 298.15 \text{ K}$) and R is the molar gas constant.

A comprehensive discussion of the available thermochemical data on 1,3-propanediol we performed in 2007 [4]. A general good agreement was observed for the available in the literature absolute vapour pressures. In the meantime, an extended GC-correlation study of α,ω -alkanediols was published by Chickos *et al.* [13], as well as a very careful vapour pressure measurements were reported from the static method just recently [14]. We also overlooked in reference [4] vapour pressures measured by ebulliometry [15] and by the thermogravimetry [16].

The vapour pressures omitted were in good agreement (except for [16]) with our previous transpiration result [4]. But it has turned out that new vapour pressures measured by static method recently [14] were slightly higher (see figure S1) in comparison to our published transpiration results [4]. In order to ascertain a vapour pressure dataset, in this work we have repeated transpiration experiments on 1,3-propanediol especially at temperatures above 333 K where the discrepancies were more apparent. However, the additional experiment has been entirely consistent with our previous transpiration study and we treated our new and old transpiration results together (see table 2).

Taking the very good agreement between vapour pressure values reported in this work and those in the literature into account (see figure S2), all available experimental values were regressed together using equation (2) to develop correlations accurately describing the vapour pressure of 1,3-propanediol over a temperature range from (292 to 717) K (see table S3):

$$\ln(p/\text{Pa}) = \frac{307.15}{R} - \frac{89069.93}{R \cdot (T/K)} - \frac{56.5}{R} \ln\left(\frac{T/K}{298.15}\right). \quad (3)$$

TABLE 2

Compilation of values of enthalpies of vaporisation $\Delta_1^g H_m^\circ$ of 1,3-propanediol.

Method ^a	T-range/K	$\Delta_1^g H_m^\circ (T_{av})/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_1^g H_m^\circ (T = 298.15 \text{ K})^b/\text{kJ} \cdot \text{mol}^{-1}$	Reference
E	383 to 433	63.3 ± 1.5	69.5 ± 1.6	[40]
	433 to 488	60.4 ± 1.5	69.6 ± 1.8	[40]
S	373 to 488	57.8 ± 2.0	(65.3 ± 2.2)	[41]
N/A	332.5 to 487.3	56.8 ± 2.0	(63.2 ± 2.1)	[42]
C	298.15		72.4 ± 0.3	[25]
E	367.3 to 489.0	64.1 ± 0.4	71.4 ± 0.8	[43]
E	401.7 to 488.1	61.8 ± 0.3	70.1 ± 0.8	[44]
E	314 to 460	61.6 ± 1.5	(66.6 ± 1.6)	[17]
N/A	332 to 488	62.6 ± 3.0	68.9 ± 3.1	[45]
E	413.4 to 458.4	62.8 ± 0.5	70.6 ± 0.9	[46]
	417.7 to 487.6	61.5 ± 0.5	70.1 ± 1.0	[15]
LRTF	480 to 716	52.2 ± 0.3	69.1 ± 1.6	[47]
GC	298.15		69.8 ± 1.1	[13]
	298.15		69.5 ± 1.7	[13]
TGA	353 to 383	80.3	(84.2)	[16]
	293.5 to 342.3		70.5 ± 0.2	[4]
S	313.2 to 461.9	67.1 ± 0.2	71.7 ± 0.5	[14]
T	292.5 to 346.4	69.4 ± 0.2	70.5 ± 0.3	This work
			71.2 ± 0.2 ^c	
				Average

^a Methods: E = Ebulliometry; T = transpiration; S = static method; C = calorimetry; GC = correlation gas-chromatography; LRTF = Low Residence Time Flow method; TGA = thermogravimetry.

^b Vapour pressure available in the literature were treated using equations (2) and (5) in order to evaluate enthalpy of vaporisation at $T = 298.15 \text{ K}$ in the same way as our own results in table 1.

^c Weighted mean value. Values in brackets were excluded from the calculation.

TABLE 3

Results for combustion experiments at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$) of the 1,3-propanediol.^a

$m(\text{substance})/\text{g}$	0.440903	0.447983	0.450193	0.443758	0.472204	0.415737
$m'(\text{cotton})/\text{g}$	0.000882	0.000954	0.000903	0.001118	0.000848	0.000984
$m''(\text{polyethene})/\text{g}$	0.302544	0.308041	0.29969	0.29898	0.307476	0.290421
$\Delta T_c/\text{K}$	1.66165	1.68962	1.66952	1.6556	1.72762	1.58503
$(e_{\text{calor}})(-\Delta T_c)/\text{J}$	-24717.1	-25133.1	-24834.2	-24627.2	-25698.5	-23577.4
$(e_{\text{cont}})(-\Delta T_c)/\text{J}$	-28.07	-28.49	-28.02	-27.89	-29.24	-26.46
$\Delta U_{\text{decomp}} \text{HNO}_3/\text{J}$	48.98	47.78	43.6	46.59	49.87	46.59
$\Delta U_{\text{corr}}/\text{J}$	7.53	7.68	7.58	7.51	7.87	7.09
$-m' \cdot \Delta_c u'/\text{J}$	14.95	16.17	15.30	18.94	14.37	16.67
$-m'' \cdot \Delta_c u''/\text{J}$	14025.12	14279.95	13892.82	13859.91	14253.76	13463.13
$\Delta_c u^\circ (\text{liq})/(\text{J} \cdot \text{g}^{-1})$	-24151.8	-24130.4	-24218.4	-24162.1	-24146	-24222.9
$-\Delta_c u^\circ (\text{liq})/(\text{J} \cdot \text{g}^{-1})$	24171.9					
$u(\Delta_c u^\circ)/\text{J} \cdot \text{g}^{-1}$	16.0 ^b					

^a The definition of the symbols assigned according to reference [29] is as follows: $m(\text{substance})$, $m'(\text{cotton})$ and $m''(\text{polythene})$ are, respectively, the mass of compound burnt, the mass of fuse (cotton), and the mass of polyethylene bag used in each experiment, masses were corrected for buoyancy; $V(\text{bomb}) = 0.32 \text{ dm}^3$ is the internal volume of the calorimetric bomb; $p^i(\text{gas}) = 3.00 \text{ MPa}$ is the initial oxygen pressure in the bomb; $m^i(\text{H}_2\text{O}) = 1.00 \text{ g}$ is the mass of water added to the bomb for dissolution of combustion gases; $e_{\text{calor}} = (14875.0 \pm 0.95) \text{ J} \cdot \text{K}^{-1}$ is the energy equivalent of the calorimeter; $\Delta T_c = T^f - T^i + \Delta T_{\text{corr}}$ is the corrected temperature rise from initial temperature T^i to final temperature T^f , with the correction ΔT_{corr} for heat exchange during the experiment; e_{cont} is the energy equivalents of the bomb contents in their initial e_{cont}^i and final states e_{cont}^f , the contribution for the bomb content is calculated with $(e_{\text{cont}})(-\Delta T_c) = (e_{\text{cont}}^i)(T^i - 298.15) + (e_{\text{cont}}^f)(T = 298.15 - T^f + \Delta T_{\text{corr}})$. $\Delta U_{\text{decomp}} \text{HNO}_3$ is the energy correction for the nitric acid formation. ΔU_{corr} is the correction to standard states.

^b Uncertainties in this table are expressed as the standard deviation of the mean.

Three data sets available from Stull [42], Stephenson and Malanowski [45], and Daubert *et al.* [17] were inconsistent with the general trend and they were rejected. As a matter of fact, these comprehensive compilations contain only approximation coefficients and not experimental vapour pressure data. Moreover, the origin of the values presented there is not clear, methods of measurements are unknown, as well as errors of measurements and purities of compounds. Embarrassingly, the set of vapour pressures recommended for the chemical-engineering calculations by DIPPR database [17] was in the low-temperature range completely out of the general trend. For this reason, the equation (3) developed in this work from the consistent data sets and for the broad temperature range should be used for the practical applications instead of those from Daubert *et al.* [17]. Moreover, our consistent dataset could be integrated into the DIPPR database, where the thermophysical properties of alkanediols were evaluated just recently [18].

Vapour pressure temperature dependences are also often fitted by the Clarke and Glew equation [19]:

$$R \ln \left(\frac{p}{p^\circ} \right) = -\frac{\Delta_1^g G_m^\circ(\theta)}{\theta} + \Delta_1^g H_m^\circ(\theta) \left(\frac{1}{\theta} - \frac{1}{T} \right) + \Delta_1^g C_{p,m}^\circ(\theta) \left[\frac{\theta}{T} - 1 + \ln \left(\frac{T}{\theta} \right) \right], \quad (4)$$

where p is the vapour pressure at the temperature T , p° is an arbitrary reference pressure ($p^\circ = 10^5 \text{ Pa}$ in this work), θ is an arbitrary reference temperature (in this work we use $\theta = 298.15 \text{ K}$ or θ was an average temperature of the experimental range), R is the molar gas constant, $\Delta_1^g G_m^\circ(\theta)$ is the difference in the standard molar Gibbs free energy between the gaseous and the liquid phases at the selected reference temperature, $\Delta_1^g H_m^\circ(\theta)$ is the difference in the standard molar enthalpy between the gas and the liquid phases, and $\Delta_1^g C_{p,m}^\circ(\theta)$ is the difference in the molar heat capacity at constant pressure between the gaseous and the liquid phase. An advantage of the Clarke and Glew equation is that the fitting coefficients (in contrast to equation (2)) are directly related to the thermodynamic functions

of vaporisation. Using the selected dataset (see [table S4](#)), the following thermodynamic functions of vaporisation were derived: $\Delta_f^{\circ}C_{p,m}^{\circ}(T = 298.15 \text{ K}) = (26.0 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f^{\circ}H_m^{\circ}(T = 298.15 \text{ K}) = (72.5 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_f^{\circ}C_{p,m}^{\circ}(T = 298.15 \text{ K}) = -(68.4 \pm 8.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

3.2. Vaporisation enthalpy of 1,3-propanediol

In this work the vaporisation enthalpy at temperature T was derived indirectly from the temperature dependence of vapour pressures measured by the transpiration using equation (5):

$$\Delta_f^{\circ}H_m^{\circ}(T) = -b + \Delta_f^{\circ}C_{p,m}^{\circ} \cdot T. \quad (5)$$

Value of $\Delta_f^{\circ}C_{p,m}^{\circ} = -(56.5 \pm 7.9) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ has been calculated according to the procedure developed by Chickos and Acree [20] based on the experimental isobaric molar heat capacity $C_{p,m}^{\circ}(1, T = 298.15 \text{ K}) = (176.5 \pm 0.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ averaged from the four results reported in [7,21–23]. It should be noted, that the value of $\Delta_f^{\circ}C_{p,m}^{\circ}$ calculated by the Chickos and Acree [20] method was in reasonable agreement with the fitting parameter $\Delta_f^{\circ}C_{p,m}^{\circ} = -(68.4 \pm 8.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ of the Clarke and Glew equation (4). Experimental absolute vapour pressures for 1,3-propanediol from the transpiration method and coefficients a and b of equation (2) are given in [table 1](#). The procedure for calculation of the combined uncertainties of the vaporisation enthalpy was described elsewhere [24]. They include uncertainties from the transpiration experimental conditions, uncertainties of vapour pressure, and uncertainties from temperature adjustment to $T = 298.15 \text{ K}$.

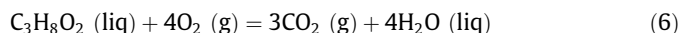
In this study, we also treated the experimental literature data omitted using equations (2) and (5) and calculated $\Delta_f^{\circ}H_m^{\circ}(T = 298.15 \text{ K})$ for the sake of comparison with our results (see [table 2](#)). Also in addition to our previous study, we recalculated uncertainties of the literature values using the same procedure [24] as it was applied for own results. Uncertainties ascribed to the literature values include new uncertainties from the experimental conditions, uncertainties of vapour pressure, and uncertainties from temperature adjustment to $T = 298.15 \text{ K}$.

The overlooked vaporisation enthalpies involved into the discussion in this study are in good agreement with our transpiration results (see [table 2](#)). In fact, from 16 entries for vaporisation enthalpies $\Delta_f^{\circ}H_m^{\circ}(T = 298.15 \text{ K})$, most of results were close to $70 \text{ kJ} \cdot \text{mol}^{-1}$ within the boundaries of experimental uncertainties of $(1 \text{ to } 3) \text{ kJ} \cdot \text{mol}^{-1}$. Similar to our previous observation for 1,2-propanediol [9], the direct calorimetric result for 1,3-propanediol $\Delta_f^{\circ}H_m^{\circ}(T = 298.15 \text{ K}) = (72.4 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$, measured by Knauth and Sabbah [25] with a Tian-Calvet calorimeter equipped with a Knudsen effusion cell, differs from the recent static and transpiration results significantly. A commercial sample of 1,3-propanediol (98%, Aldrich) used by Knauth and Sabbah [25] was purified additionally by fractional distillation over a rotating band column with 30 theoretical plates. The mole-fraction purity of the sample was checked by low-temperature DTA using the freezing-temperature method. The final purity for 1,3-propanediol was (0.9923 ± 0.0002) [25]. Taking into account the hygroscopic nature of alkanediols, it is plausible that the disagreement of calorimetric values with other available results is due traces of moisture, as well as due to insufficient purity of the sample. In comparison to calorimetric experiment, the transpiration technique used in our lab offers two advantages [10]. The first advantage is the possibility to withdraw moisture and volatile impurities in preliminary experiments by flashing the sample with dry nitrogen (conditioning of the sample) and the resulting constant sample vapour pressure indicates that all moisture has been withdrawn. The second

advantage arises from being able to measure the vapour pressures near the reference temperature $T = 298.15 \text{ K}$, and, consequently, being able to minimise extrapolation error by obtaining vaporisation enthalpy at this temperature. The molar enthalpy of vaporisation of 1,3-propanediol $\Delta_f^{\circ}H_m^{\circ}(T = 298.15 \text{ K}) = (70.5 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$ was measured in this work around the $T = 298.15 \text{ K}$ (see [table 1](#)) and this value is less affected due to adjusting to the reference temperature in comparison to the ebulliometric and static results. This new value is also in perfect agreement with our previous result measured using the same technique [4] (see [table 2](#)). However, in order to establish more confidence, we calculated the weighted mean value $\Delta_f^{\circ}H_m^{\circ}(T = 298.15 \text{ K}) = (71.2 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$ for 1,3-propanediol using 14 entries from [table 2](#). Uncertainties of the values are listed in [table 2](#) where used as the weighting factor. This averaged result has been recommended for further thermochemical calculations. It should be noted that the value $\Delta_f^{\circ}H_m^{\circ}(T = 298.15 \text{ K}) = (72.5 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$, derived as the fitting parameter of the Clarke and Glew equation is slightly higher than that of our recommendation. This disagreement is still acceptable, taking into account that fitting of equation (4) was performed over the temperature range (292 to 717) K, where vapour pressures at high temperatures dominate.

3.3. The enthalpy of formation from the combustion calorimetry

Results of combustion experiments on 1,3-propanediol are given in [table 3](#). The relative atomic masses used for the elements C, H, N and O were calculated as the mean of the bounds of the interval of the standard atomic weights recommended by the IUPAC commission in 2011 [26] for each of these elements. The value of the standard specific energy of combustion $\Delta_c u^{\circ} = -(24171.9 \pm 16.0) \text{ J} \cdot \text{g}^{-1}$ has been used to derive the standard molar enthalpy of combustion $\Delta_c H_m^{\circ} = -(1841.8 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$, and the standard molar enthalpy of formation in the liquid state $\Delta_f H_m^{\circ}(l) = -(482.0 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$. Values of $\Delta_c u^{\circ}$ and $\Delta_c H_m^{\circ}$ refer to the reaction:



The enthalpy of formation $\Delta_f H_m^{\circ}(l)$ of the 1,3-propanediol was calculated from the enthalpic balance according to equation (6) using standard molar enthalpies of formation of $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ recommended by CODATA [27]. Uncertainties related to combustion experiments were calculated according to the guidelines presented in [28,29]. The uncertainties of the standard molar energy and enthalpy of combustion correspond to expanded uncertainties of the mean (0.95 level of confidence) and include the contribution from the calibration with benzoic acid and from the values of the auxiliary quantities used. The uncertainty assigned to $\Delta_f H_m^{\circ}(l)$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2 .

Standard molar enthalpies of formation of 1,3-propanediol were measured using the combustion calorimetry earlier [5–7]. The first result $\Delta_f H_m^{\circ}(l) = -(464.6 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$ reported by Gardner and Hussain [5] was in significant disagreement with the value reported by Knauth and Sabbah [6] $\Delta_f H_m^{\circ}(l) = -(480.8 \pm 5.1) \text{ kJ} \cdot \text{mol}^{-1}$. It has turned out that Gardner and Hussain [5] failed to measure purity of 1,3-propanediol by GC due to sample decomposition in injector. Thus, they checked purity for this compound by a less sensitive refractive indices method. The most recent combustion result $\Delta_f H_m^{\circ}(l) = -(451.7 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ on 1,3-propanediol reported by Tsvetkova *et al.* [7] have brought more confusion in the current state. Analysis of the scarce experimental details reported by Tsvetkova *et al.* [7] has revealed errors in the data

TABLE 4Thermochemical data at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for 1,3-propanediol.^a

$\Delta_c H_m^\circ$ (l)/kJ · mol ⁻¹	$\Delta_f H_m^\circ$ (l)/kJ · mol ⁻¹	$\Delta_f H_m^\circ$ (g)/kJ · mol ⁻¹	$\Delta_f H_m^\circ$ (g) _{exp.} /kJ · mol ⁻¹	$\Delta_f H_m^\circ$ (g) _{G3MP2} ^{b,c} /kJ · mol ⁻¹
-1859 ± 2.3 [5]	-464.8 ± 2.5 [5]			
-1843.0 ± 5.1 [6]	-480.8 ± 5.1 [6]			
-1865.1 ± 3.0 [7]	-458.7 ± 3.0 [7]			
-1841.8 ± 2.5 ^c	-482.0 ± 2.5 ^c	70.5 ± 0.3 ^c	411.5 ± 2.5 ^c	
	-481.8 ± 2.2 ^d	71.2 ± 0.2 ^e	-410.6 ± 2.2	-410.6 ± 0.6

^a Uncertainties correspond to expanded uncertainties of the mean (0.95 level of confidence).^b From table 5.^c Results obtained in this study.^d The weighted mean value was calculated only from enthalpy of formation derived in this work and those from reference [6].^e Weighted mean value from table 2.

treatment. We recalculated from the reported standard specific energy of combustion $\Delta_c u^\circ = -(24478 \pm 18.0) \text{ J} \cdot \text{g}^{-1}$ the value $\Delta_f H_m^\circ$ (l) = $-(458.7 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$, which seems to be now comparable with the result from Gardner and Hussain [5]. However, in addition to the incorrect data treatment, the attestation of the sample purity by Tsvetkova *et al.* [7] was performed only by very insensitive elemental analysis. Thus, the spread of the available literature values by over $20 \text{ kJ} \cdot \text{mol}^{-1}$ has prompted the re-determination of combustion energy. Our new result for 1,3-propanediol, $\Delta_f H_m^\circ$ (l) = $-(482.0 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$ was close to those from Knauth and Sabbah [6]. Taking into account careful purification and purity attestation of the sample our value helps to resolve existing ambiguity. In order to establish more confidence, we calculated the weighted mean value $\Delta_f H_m^\circ$ (l) = $-(481.8 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$ for 1,3-propanediol from own result and those from Knauth and Sabbah [6]. Uncertainties of enthalpies of formation were used as the weighting factor. This averaged result has been recommended for further thermochemical calculations.

3.4. Calculation of the gaseous standard molar enthalpy of formation of 1,3-propanediol

Value of vaporisation enthalpy of 1,3-propanediol, averaged in this work (table 2) can now be used together with the averaged result from combustion calorimetry for further calculation of the gaseous standard enthalpy of formation, $\Delta_f H_m^\circ$ (g) at $T = 298.15$ K. The resulting value of $\Delta_f H_m^\circ$ (g) = $-(410.6 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$ for 1,3-propanediol is given in table 4. Since a significant discrepancy among available experimental enthalpies of formation for this compound has been found, any additional arguments to support the reliability of our new measurements are required. A valuable test of consistency of the experimental data could provide high-level quantum-chemical calculations [30,31]. We have used the composite method G3MP2 for calculation of the gaseous enthalpy of formation of 1,3-propanediol for comparison with the experimental data.

4. Quantum chemical calculations

4.1. Methods of calculations

Standard *ab initio* molecular orbital calculations for 1,3-propanediol conformers were performed with the Gaussian 09 series of programs [32]. Energies of compounds under study were calculated using the G3MP2 level [33]. Initial search for stable conformers was performed using force field method MM3 [34]. Enthalpies of 1,3-propanediol conformers were based on the electronic energy calculations obtained by the G3MP2 method using standard procedures of statistical thermodynamics [35]. Details on computational procedure are given in our previous paper [31].

4.2. Conformational equilibrium and relative energies of 1,3-propanediol conformers

A preliminary study of conformational equilibrium of 1,3-propanediol was important for a correct calculation of $\Delta_f H_m^\circ$ (g). From 23 available conformers [36] we selected only 9 most stable conformers in the 1,3-propanediol molecule (see table S4 in Supplementary data). The energy differences of conformers related to the most stable conformer (St) are given in table 5 and in table S4 (Supplementary data). There were three conformers with very close energetics (within $2 \text{ kJ} \cdot \text{mol}^{-1}$). Other five conformers were about (5 to 9) $\text{kJ} \cdot \text{mol}^{-1}$ less stable. The thermal population P_i of the conformers at $T = 298.15$ K was calculated by equations:

$$P_i = \frac{e^{-\frac{\Delta G_i}{RT}}}{1 + \sum_{i=1}^n e^{-\frac{\Delta G_i}{RT}}}; \quad \text{with} \quad \Delta G_i = G_i - G_{\text{St}}, \quad (7)$$

where the Gibbs free energy G_{St} was referred to the most stable conformer. The thermal population was taken into account for calculation of the energy and enthalpy of the equilibrium mixture of conformers (table S4 in Supplementary data) and it was finally applied for calculation of theoretical gaseous enthalpy of formation, $\Delta_f H_m^\circ$ (g), of 1,3-propanediol (see table 4, last column).

4.3. Mutual validation of experimental and theoretical enthalpy of formation of 1,3-propanediol

After our additional studies of 1,3-ethanediol the available experimental values $\Delta_f H_m^\circ$ (l) could be divided in two groups. The first one is around $-465 \text{ kJ} \cdot \text{mol}^{-1}$ from references [5,7], and the second group with the level of $-480 \text{ kJ} \cdot \text{mol}^{-1}$ from Knauth and Sabbah [6] and from the current work (see table 4). Our recent experiences with the high-level quantum-chemical calculations [30,31,37–39] provide us a confidence to resolve the contradictions with 1,3-propanediol by using any suitable composite method, *e.g.* the G3MP2. The relatively small size together with the manageable amount of flexible conformers makes this molecules particularly good candidate for accurate theoretical calculation of ideal gas properties. Demonstration of agreement between the independent experimental and computed results can provide strong validation for both results and to establish thermochemical data for 1,3-propanediol of the benchmark quality.

Results from extended conformational analysis performed for 1,3-propanediol performed for nine conformers at the G3MP2 level of theory (table S4 in Supplementary data) were used to derive the theoretical value of the standard molar enthalpy of formation $\Delta_f H_m^\circ$ (g, $T = 298.15$ K) in the gaseous phase.

Enthalpies H_{298} calculated by the G3MP2 for conformers of 1,3-propanediol were converted to enthalpies of formation $\Delta_f H_m^\circ$ (g, $T = 298.15$ K) using the conventional atomization reaction:

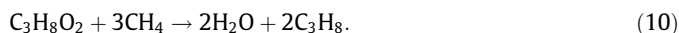
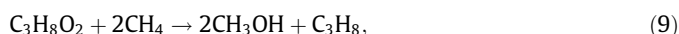
TABLE 5

Conformational analysis for 1,3-propanediol: Gibbs free energies, ΔG_{298} , mole fractions of conformer, x_i , and enthalpies of formation conformers, $\Delta_f H_m^\circ$ at $T = 298.15$ K.

1	$\Delta G_{298}/\text{kJ} \cdot \text{mol}^{-1}$ 2	$\exp(-\Delta G_{298}/RT)$ 3	x_i 4	$\Delta_f H_m^\circ$ (8)/ $\text{kJ} \cdot \text{mol}^{-1}$ 5	$\Delta_f H_m^\circ$ (AT) ^a / $\text{kJ} \cdot \text{mol}^{-1}$ 6	$\Delta_f H_m^\circ$ (9)/ $\text{kJ} \cdot \text{mol}^{-1}$ 7	$\Delta_f H_m^\circ$ (10)/ $\text{kJ} \cdot \text{mol}^{-1}$ 8
1	1.79	0.49	0.0992	−408.7	−411.5	−412.1	−412.7
2	1.79	0.49	0.0992	−408.7	−411.5	−412.1	−412.7
3	0.00	1.00	0.2043	−409.9	−412.7	−413.3	−413.9
4	0.00	1.00	0.2043	−409.9	−412.7	−413.3	−413.9
5	5.24	0.12	0.0247	−402	−404.7	−405.4	−406
6	5.24	0.12	0.0247	−402	−404.7	−405.4	−406
7	4.46	0.17	0.0338	−404	−406.7	−407.4	−408
8	4.46	0.17	0.0338	−404	−406.7	−407.4	−408
9	2.03	0.44	0.0901	−405.5	−408.3	−408.9	−409.5
10	2.03	0.44	0.0901	−405.5	−408.3	−408.9	−409.5
11	8.81	0.03	0.0058	−397.7	−400.3	−401.1	−401.7
12	6.07	0.09	0.0177	−401.3	−404	−404.7	−405.3
13	6.07	0.09	0.0177	−401.3	−404	−404.7	−405.3
14	5.64	0.10	0.0210	−401.6	−404.3	−405	−405.6
15	5.64	0.10	0.0210	−401.6	−404.3	−405	−405.6
16	8.60	0.03	0.0064	−398.1	−400.7	−401.5	−402.1
17	8.60	0.03	0.0064	−398.1	−400.7	−401.5	−402.1
				−407.2 ^b	−410.0 ^b	−410.6 ^b	−411.2 ^b

Average: ^c $\Delta_f H_m^\circ = -410.6 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$ ^a Calculated according to equation (11).^b Calculated according to equation (7).^c The average value was calculated from the bold entries in columns 6–8.

as well as with two isodesmic reactions:



Using enthalpies of reactions (8)–(10), calculated by the G3MP2, together with the literature data for $\Delta_f H_m^\circ$ ($g, T = 298.15$ K) of methane, methanol, and *n*-propane from reference [48] and water [27], enthalpies of formation for nine 1,3-propanediol conformers were calculated (see table 4). The composition of the equilibrium conformers was derived with help of equation (7). Enthalpies of formation calculated from isodesmic reactions (9) and (10) were in very close agreement (see columns 7 and 8 in table 5). However, the enthalpy of formation of 1,3-propanediol calculated from atomization procedure (equation (8)) was slightly lower than those from isodesmic reactions. Similar deviations have been observed for different series of compounds systematically [30,31,37]. In order to refine the atomisation results and provide an alternative approach to isodesmic reactions, a simple correction procedure has been suggested in our recent work [30]. We observed the simple linear-type correlation between experimental enthalpies of formation and those calculated by the standard atomisation procedure. In this work, we have used the restricted data set collected for 8 *n*-alcohols and alkanediols (see table S5) in order to derive the following linear correlations:

$$\Delta_f H_m^\circ (g)_{\text{exp}} / \text{kJ} \cdot \text{mol}^{-1} = (1.017 \pm 0.007) \cdot \Delta_f H_m^\circ (g)_{\text{G3MP2}} + (4.0 \pm 1.0) \quad \text{with} \quad R^2 = 0.9989. \quad (11)$$

With these correlation we calculated “corrected” enthalpies of formation of 1,3-propanediol conformers (column 6, table 5). As

can be seen from this table the “corrected” average value from atomisation reaction (8) provides good agreement with those from both isodesmic reactions (columns 7 and 8, table 5). In our opinion, the combination of the quantum-chemical methods with such a “corrected” atomization procedure is generally recommended for reliable calculations of $\Delta_f H_m^\circ$ ($g, T = 298.15$ K) of organic compounds in addition to the conventional isodesmic reactions. Taking into account the excellent agreement of enthalpies of formation calculated according to reactions (8)–(10), we averaged these computed values and derived the theoretical value of $\Delta_f H_m^\circ (g)_{\text{G3MP2}} = -(410.6 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$ for the favourable comparison with the experimental value $\Delta_f H_m^\circ (g)_{\text{exp}} = -(410.6 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$. The latter value was derived as the sum of the evaluated vaporisation enthalpy (see table 2) and the weighted average of the combustion result measured by Knauth and Sabbah [6] and those from the current work (see table 4). Now, having established good consistency of the experimental gas-phase enthalpy of formation and the theoretical value, $\Delta_f H_m^\circ (g)_{\text{G3MP2}}$, for 1,3-propanediol, we are able to recommend the evaluated experimental properties at $T = 298.15$ K (see table 4): $\Delta_f H_m^\circ (g) = -(410.6 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^\circ (l) = -(481.8 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_f^\circ H_m^\circ = (71.2 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$ as the reliable benchmark properties for further thermochemical calculations. We suggest the value of $\Delta_f H_m^\circ (g)$ for validation of sophisticated quantum-chemical methods. Moreover, we can apply the value of $\Delta_f H_m^\circ (l)$ for evaluation of the experimental results available in the literature. For example, a very interesting series of equilibrium studies of acetals and ketals were published by Anteunis *et al.* [49,50]. Reviewing these studies in the previous work [51], it was not possible to assess reliability of the reaction enthalpy $\Delta_r H_m^\circ = -(23.0 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$ [49] measured by using the NMR-spectroscopy for the following reaction:

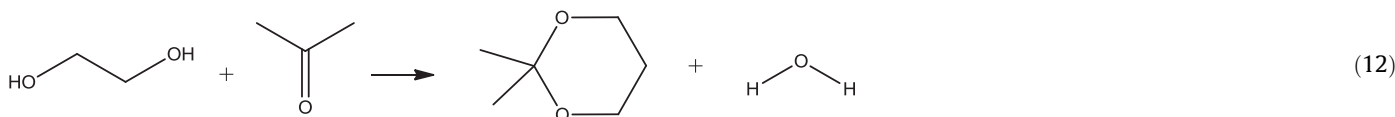


TABLE 6

Standard molar thermodynamic properties of 1,3-propanediol at $T = 298.15$ K.

State	$\Delta_f H_m^\circ$ kJ · mol ⁻¹	$\Delta_f S_m^\circ$ J · K ⁻¹ · mol ⁻¹	$\Delta_f^\circ C_m^\circ$ kJ · mol ⁻¹	S_m° J · K ⁻¹ · mol ⁻¹	$C_{p,m}^\circ$
Liquid	-481.8 ± 2.2	-548.4 ± 0.3	-318.3 ± 2.2	196.1 ± 0.1 [7,22]	176.5 ± 0.2
Gas	-410.6 ± 2.2	-399.2 ± 0.7	-291.6 ± 2.2	345.5 ± 0.6 ^a	108.1 ± 8.1 ^b

^a Calculated as sum of S_m° (l) from this table and entropy of vaporisation $\Delta_f^\circ S_m^\circ$ ($T = 298.15$ K) = (149.4 ± 0.6) J · K⁻¹ · mol⁻¹ adjusted to the reference temperature by fitting vapour pressures with equation (2).

^b Calculated as sum of $C_{p,m}^\circ$ (l) from this table and contribution $\Delta_f^\circ C_{p,m}^\circ = -(68.4 ± 8.1)$ J · K⁻¹ · mol⁻¹ from the Clarke and Glew equation (4).

We failed in the past [51] to validate this result due to the ambiguity of the $\Delta_f H_m^\circ$ (l)-value for 1,3-propanediol. Having now the evaluated enthalpy of formation of 1,3-propanediol (table 4) together with the literature data for 2,2-dimethyl-1,3-dioxane (CAS 695-30-7) $\Delta_f H_m^\circ$ (l) = -(468.9 ± 2.1) kJ · mol⁻¹ [52], acetone $\Delta_f H_m^\circ$ (l) = -(248.1 ± 0.7) kJ · mol⁻¹ [48], and water $\Delta_f H_m^\circ$ (l) = -(285.83 ± 0.04) kJ · mol⁻¹ [27], we calculated $\Delta_f H_m^\circ$ = -(24.8 ± 3.1) kJ · mol⁻¹ for the reaction (10). A fair agreement between the experimental reaction enthalpy by Anteunis *et al.* [49] and our estimate increase the confidence of the extended dataset for acetals and ketals measured in this laboratory.

4.4. Mutual validation of experimental and theoretical entropy of 1,3-propanediol

The possibility to derive ideal gas properties of organic compounds solely from computational methods would provide numerous key values for material sciences, engineering, and biochemistry. A feasibility of chemical processes is governed by the sign of the Gibbs free energy, $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \cdot \Delta_f S_m^\circ$, which is highly desirable to assess from the computational chemistry. There is a definite progress in the reliable enthalpy calculations with different composite methods [37–39]. However, in comparison to the enthalpy, H_{298} , the quantum-chemical calculations of the entropy are significantly more sophisticated and challenging. Nevertheless, a systematic study of ability of *ab initio* methods for reliable prediction of standard molar entropy, S_m° (g), of organic molecules in the gas state should be performed. Mutual validation of experimental and theoretical entropy of 1,3-propanediol can be a valuable attempt to collect experiences. In this work we calculated the theoretical entropy, S_m° (g, $T = 298.15$ K)_{G3MP2} = 316.8 J · K⁻¹ · mol⁻¹ using the G3MP2 method, where the optimisation and frequency calculation was performed at the HF/6-31G(d) level of theory. Admittedly, the latter method has not been the best for the careful frequency calculations, but it has been incorporated as the standard first step in the G3MP2 composite method. In order to get the experimental value of S_m° (g, $T = 298.15$ K)_{exp}, we used the literature values for the standard molar entropy S_m° (l, $T = 298.15$ K)_{exp} = (196.1 ± 0.1) J · K⁻¹ · mol⁻¹ measured in the liquid phase by using adiabatic calorimetry [7,22]. It is important to note, that values of S_m° (l, $T = 298.15$ K)_{exp} measured in two different laboratories [7,22] are indistinguishable. The experimental value of the molar vaporisation entropy $\Delta_f^\circ S_m^\circ$ ($T = 298.15$ K) = (149.4 ± 0.6) J · K⁻¹ · mol⁻¹ was derived from the temperature dependence of vapour pressures, measured by the transpiration method (see tables 1 and 6). Summing up both contributions, we calculated the experimental standard molar entropy S_m° (g, $T = 298.15$ K)_{exp} = (345.5 ± 0.6) J · K⁻¹ · mol⁻¹. The difference of $T = 28.7$ J · K⁻¹ · mol⁻¹ between experiment and theory cannot be explained only by inaccuracy of the HF/6-31G(d) level of theory. It was well established [53], that flexible molecules require a careful account for the conformational contributions to the entropy $\Delta_{\text{conf}} S_m^\circ$ (g, $T = 298.15$ K). The conformational contributions to the

entropy in the gas state at $T = 298.15$ K were assessed using equation [53]:

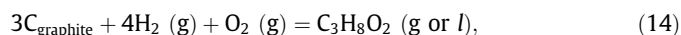
$$\Delta_{\text{conf}} S_m^\circ = -R \cdot \sum_{i=1}^n x_i \cdot \ln x_i. \quad (13)$$

Using the mole fractions of nine conformers x_i given in table 5 and also taking into account their optical isomers, the contribution $\Delta_{\text{conf}} S_m^\circ$ (g, $T = 298.15$ K) = 19.6 J · K⁻¹ · mol⁻¹ was estimated and added to the G3MP2 calculated entropy: S_m° (g, $T = 298.15$ K)_{G3MP2} = (316.8 + 19.6) = 336.4 J · K⁻¹ · mol⁻¹. Thus, additional conformational contributions have brought the theory closer to the experiment. Drawing conclusion from this comparison, we could generally approve ability of the G3MP2 method to provide acceptable values of standard molar entropies. It seems to be that for the reasonable level of the S_m° (g)-values could be achieved for the simple feasibility calculations of miscellaneous chemical and biological processes.

5. Standard molar thermodynamic functions of 1,3-propanediol

Due to recent developments of the “green chemistry” 1,3-propanediol was considered as the large scale platform chemical produced from a glucose fermentation processes [54]. Thermodynamic modelling and optimisation of 1,3-propanediol processes requires knowledge of basic thermodynamic functions for this molecule. This paper has contributed with the evaluated energetic and entropic properties of 1,3-propanediol. We have compiled available experimental values and calculated thermodynamic functions of formation for 1,3-propanediol listed in table 6.

The entropy of formation, $\Delta_f S_m^\circ$, was calculated on the basis of reaction (14):



using the values given in table 6 and the values of entropy of formation for C_{graphite} (5.74 ± 0.13) J · K⁻¹ · mol⁻¹, for H_2 (g) (130.52 ± 0.02) J · K⁻¹ · mol⁻¹, and for O_2 (g) (205.04 ± 0.03) J · K⁻¹ · mol⁻¹ recommended in [55]. The Gibbs function of formation, $\Delta_f G_m^\circ$, was estimated from the values of $\Delta_f H_m^\circ$ and $\Delta_f S_m^\circ$ (see table 6). The standard molar thermodynamic functions in the liquid and in the gas phase collected in table 6 can be used for optimisation of 1,3-propanediol processing into further valuable bio-based platform chemicals

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2015.01.014>.

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