ISSN 2686-7575 (Online)

https://doi.org/10.32362/2410-6593-2020-15-1-28-36

UDC 544.31; 544.27; 544.22

Thermodynamic properties of L-menthol in crystalline and gaseous states

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Objectives. *Menthol causes a cooling sensation and reduces the nerve activity when it is applied locally, ingested, or inhaled. This feature explains its extensive use as both an aromatizer and a flavoring agent in food manufacturing, tobacco industry, cosmetics production, as well as a mild anesthetic and antiseptic in dentistry. This work aimed to perform a comprehensive thermodynamic study of L-menthol in both crystalline and gaseous states.*

Methods. *To determine the combustion energy of L-menthol in the crystalline state, combustion bomb calorimetry was used. The temperature dependence of L-menthol's heat capacity in the range of 5–370 K and the melting (fusion) parameters were determined using adiabatic calorimetry. Quantum chemical calculations were performed on a standalone virtual machine in the Google Cloud Platform using an eight-core Intel Xeon Scalable Processor (Skylake) with a 2.0 GHz (up to 2.7 GHz at peak load) clock frequency and 8 GB RAM.*

Results. *The energy and enthalpy of L-menthol combustion in the crystalline state were determined, and the standard enthalpy of L-menthol formation in the gaseous state was calculated using the standard enthalpy of sublimation. The standard thermodynamic functions (reduced enthalpy, entropy, and reduced Gibbs energy) of L-menthol in both crystalline and liquid states were obtained based on the smoothed values of heat capacity and melting parameters. The group of isodesmic reactions for the ab initio calculation of the enthalpy of formation for gaseous L-menthol was substantiated. Electronic energy and frequencies of normal modes of the molecules involved in these reactions were calculated using the Gaussian 4 composite quantum chemical method. Further, the sublimation enthalpy of L-menthol was calculated using the extended Politzer equation according to the electrostatic potential model.*

Conclusions. *The first comprehensive thermodynamic study of L-menthol in various states of aggregation was performed, and the values calculated using semiempirical methods were consistent with the experimental values within error limits, which confirms the reliability of the results.*

Keywords: *L-menthol, thermodynamic properties, calorimetry, heat capacity, enthalpy of formation, phase transition parameters, quantum chemical calculations.*

For citation: Blokhin A.V., Yurkshtovich Ya.N. Thermodynamic properties of L-menthol in crystalline and gaseous states. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2020;15(1):28-36. https://doi.org/10.32362/2410-6593-2020-15-1-28-36

Термодинамические свойства L-ментола в кристаллическом и газообразном состояниях

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Цели. *Ментол при местном воздействии, употреблении в пищу или вдыхании вызывает ощущение охлаждения и снижает нервную активность, что объясняет его широкое применение в качестве отдушки и вкусовой добавки в пищевой и табачной промышленности, косметике, а также в качестве мягкого анестетика и антисептика в стоматологии. Цель работы заключалась в комплексном термодинамическом исследовании L-ментола в кристаллическом и газообразном состояниях.*
Методы. *Методом бомбовой калориметрии сгорания была определена энергия сгорания L-ментола в кристаллическом состоянии. Методом адиабатической калориметрии была получена температурная зависимость теплоемкости L-ментола в интервале 5–370 К и найдены его параметры плавления. Квантово-химические вычисления производились на выделенной виртуальной машине в облачном сервисе Google Cloud Platform с использованием 8 вычислительных ядер Intel Xeon Scalable Processor (Skylake) с тактовой частотой 2.0 ГГц (до 2.7 ГГц при пиковой нагрузке) и 8 ГБ оперативной памяти.*
Результаты. *Были определены энергия и энтальпия сгорания L-ментола в кристаллическом состоянии. С использованием величины стандартной энтальпии сублимации был выполнен расчет стандартной энтальпии образования L-ментола в газообразном состоянии. На основании сглаженных значений теплоемкости и параметров плавления получены стандартные термодинамические функции (приведенная энтальпия, энтропия и приведенная энергия Гиббса) L-ментола в кристаллическом и жидком состояниях. Обоснована группа изодесмических реакций для ab initio расчета энтальпии образования газообразного L-ментола, и с использованием композитного квантово-химического метода Gaussian 4 вычислены электронная энергия и частоты нормальных колебаний молекул–участников этих реакций. В рамках модели электростатического потенциала по расширенному уравнению Политцера рассчитана энтальпия сублимации L-ментола.*
Выводы. *Впервые было проведено комплексное термодинамическое исследование L-ментола в различных агрегатных состояниях. Величины, рассчитанные с помощью полуэмпирических методов, согласуются в пределах погрешностей с опытными величинами, что подтверждает достоверность полученных результатов.*

Ключевые слова: *L-ментол, термодинамические свойства, калориметрия, теплоемкость, энтальпия образования, параметры фазовых переходов, квантово-химические расчеты.*

Для цитирования: Блохин А.В., Юркштович Я.Н. Термодинамические свойства L-ментола в кристаллическом и газообразном состояниях. *Тонкие химические технологии.* 2020;15(1):28-36. https://doi.org/10.32362/2410-6593-2020-15-1-28-36

INTRODUCTION

At present, one of the most important tasks in physical chemistry is identification and development of methods that can predict the properties of substances based on molecular structure. The possibility of ab initio calculation of the properties allows us to move toward the streamlined synthesis of compounds, which significantly reduces both time and cost of research.

The values of the thermodynamic properties of substances are used to calculate the thermal characteristics of reactions and a number of technological parameters, thus actualizing their determination for as many substances as possible.

Menthol causes a cooling sensation and reduces nerve activity when applied locally, ingested, or inhaled. This feature explains its extensive use as an aromatizer and a flavoring agent in food manufacturing, tobacco industry, cosmetics production, and in dentistry—as a mild anesthetic and antiseptic [1].

To determine the standard enthalpy of combustion of L-menthol in the crystalline state at T = 298.15 K, combustion bomb calorimetry was used, based on which the standard enthalpies of formation of crystalline and gaseous substances at a certain temperature were determined. Moreover, the adiabatic calorimetry method was used to examine the temperature dependence of the heat capacity of L-menthol in both crystalline and liquid states, and the temperature and enthalpy of fusion were determined. Based on the smoothed heat capacities and melting parameters, the standard thermodynamic functions of L-menthol were calculated in the temperature range of 5–370 K.

The standard enthalpy of L-menthol formation in the gaseous state was calculated using the Gaussian 4 composite quantum chemical method [2], and the sublimation enthalpy was determined using the electrostatic potential model. Furthermore, the calculated values of the formation and sublimation enthalpies agreed with the experimental values within the combined error of their determination.

MATERIALS AND METHODS

The sample of L-menthol was provided by *Belpharmatsiya*, Belarus. Its purity (the content of L-menthol in the sample), which was determined using gas-liquid chromatography, was greater than or equal to 99.98 wt %. Fractional melting was used in two sets of experiments in an adiabatic calorimeter to determine the purity and the melting (fusion) temperature of L-menthol, and these parameters were found to be 99.73±0.02 mol % and 315.60±0.02 K, respectively. The experimental data were then approximated by a linear equation using the ordinary least squares method:

$$T = T_{\mathrm{fus}} - \frac{RT_{\mathrm{fus}}^{2}\left(1-x\right)}{\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\circ}}\frac{1}{f}, \qquad (1)$$

where $(1 - x)$ is the molar fraction of impurities in the initial sample; f is the equilibrium fraction of the melt at a temperature T (equal to the ratio of the heat already used to melt the sample to the total fusion heat of the substance); and $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\circ}$ ($\mathrm{J{\times}mol^{-1}}$) is the fusion enthalpy of the substance at T_{fus}.

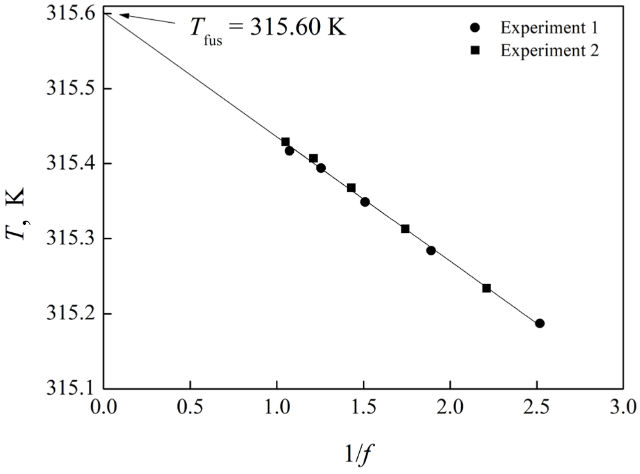

Fig. 1. Experimental results for the fractional melting of the L-menthol sample.

Figure 1 shows the dependence of the equilibrium temperature on the inverse melt fraction.

The enthalpy of L-menthol combustion was determined in an automatic isothermal-shell combustion calorimeter and a stationary self-sealing bomb (with a volume of 320 cm^3) [3, 4]. The temperature change during the experiment was recorded using a platinum resistance thermometer (R = 500 Ω). Furthermore, menthol was dried in a desiccator over phosphorus pentoxide before it was compressed into tablets, while the preparation of the substance for burning in the calorimeter was performed in the air. For the experiment, menthol was placed on a platinum wire (d = 0.05 mm) in the form of compressed tablets. Before the start of the experiment, distilled water (1 ml) was added to the calorimetric bomb to saturate the system with water vapor. The reaction was initiated by electric current and was conducted in the oxygen atmosphere at a pressure of ~30 atm.

The condensate formed in the bomb was quantitatively transferred to a beaker and titrated with 0.1 M NaOH solution to correct the results for the heat of nitrogen oxidation (this gas was an admixture in oxygen).

All data were read off the calorimeter using a computer. The initial and final periods contained 20 counts, and the main one contained 25 counts (interval between readouts 30 s). Table 1 shows the input parameters for calculating the combustion energy of menthol. The combustion energy was calculated considering the Washburn corrections [5].

Table 1. Input data for calculating the combustion energy of L-menthol

	Parameter	Value
1	Density, $\mathrm{g{\times}cm^{-3}}$	0.946
2	Heat capacity, $\mathrm{J{\times}g^{-1}{\times}K^{-1}}$	1.60045
3	$(\partial U/\partial P)_T$, $\mathrm{J{\times}MPa^{-1}{\times}g^{-1}}$	–0.106
4	Heat of vaporization of platinum wire, $\mathrm{J{\times}g^{-1}}$	–420

Heat capacities of crystalline and liquid L-menthol were in the range of 5−70 K and the parameters of melting were determined using a TAU-10 automatic vacuum adiabatic calorimeter (*Termis*, Moscow, Russia), according to a previously reported method [4, 6]. The temperature was measured with an iron–rhodium resistance thermometer (R = 50 Ω), placed on the inner surface of an adiabatic screen.

The adiabatic conditions in the calorimeter were maintained using a differential thermocouple (copper + 0.1% iron)/chromel and two heaters, i.e. the main one and the additional one, to eliminate temperature gradients over the length of the adiabatic shell. Heater control and visible energy detection, temperature measurements, and calculations of heat capacities in the calorimetric experiment were performed using the AK-6.25 automatic control unit.

A sample of the substance was placed in the air within a container (volume ~1.0 cm^3) per 4/5 of its volume, and the container with the sample was degassed in vacuum for 30 min after sample loading. To ensure the rapid establishment of thermal equilibrium during calorimetric measurements, the container (after degassing) was filled with helium at 10 kPa, and then it was hermetically sealed with a bronze lid. An indium ring was used as a sealant. The container with the sample was weighed on a Mettler-Toledo AG245 balance (with a maximum error of $\pm 5\times 10^{-5}$ g), and the hermiticity of the container was controlled by several curing cycles in the air and in vacuum to achieve a fixed mass. Liquid nitrogen was used as a refrigerant in the temperature range of 80–370 K, whereas liquid helium was used in the temperature range of 5–100 K. Error in measuring the heat capacity in the adiabatic calorimeter did not exceed ±0.4% in the range of 20–370 K, ±1% in the range of 10–20 K, and ±2% in the range of 5–10 K. The share of the sample's heat capacity in the total heat capacity of the filled calorimetric ampoule was greater than or equal to 45%.

The formation enthalpy of L-menthol in the gaseous state was calculated using the Gaussian 4 composite quantum chemical method. Total molecular energies and frequencies of normal modes were calculated using the GAUSSIAN 09 program. Calculations were performed on a standalone virtual machine in the Google Cloud Platform using an eight-core Intel Xeon Scalable Processor (Skylake) with a 2.0 GHz (up to 2.7 GHz at peak load) clock frequency and 8 GB RAM.

The sublimation enthalpy of L-menthol was determined using the extended Politzer equation, and the necessary molecular parameters of the substance were obtained using the Multiwfn 3.7 package.

RESULTS AND DISCUSSION

Based on a set of six experiments at T = 298.15 K, the standard energy and enthalpy of combustion of L-menthol in the crystalline state were as follows:

$$\Delta_c U^{\circ}_{298} = -(6304.4 \pm 1.3)\ \text{kJ}\times\text{mol}^{-1},$$
$$\Delta_c H^{\circ}_{298} = -(3615.6 \pm 1.3)\ \text{kJ}\times\text{mol}^{-1}.$$

Moreover, the standard enthalpy of menthol formation in the crystalline state is

$$\Delta_f H^{\circ}_{298}(cryst) = -(477.8 \pm 1.9)\,\text{kJ}\times\text{mol}^{-1}.$$

The standard enthalpy of menthol formation in the gaseous state at T = 298.15 K, considering the recommended value of the sublimation enthalpy $\Delta_{sub}H^{o}$ = (84.4±1.7) kJ×mol^{-1} [7], is

$$\Delta_f H^{\circ}_{298}(gas) = -(393.4 \pm 2.5)\,\text{kJ}\times\text{mol}^{-1}.$$

Figure 2 shows the dependence of the heat capacity of L-menthol in the condensed state on the temperature in the range of 5−370 K, under saturated vapor pressure. The values of relative atomic masses recommended by IUPAC [8] were used to calculate the molar heat capacities.

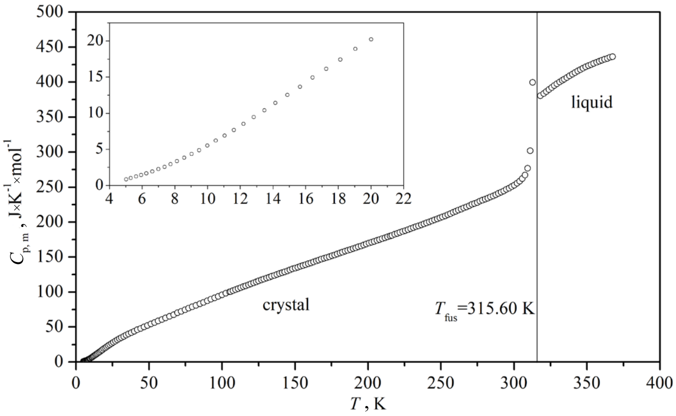

Fig. 2. Dependence of the heat capacity of L-menthol on temperature in the range of 5–370 K.

As determined in a set of four experiments at T_{fus} = 315.60 K, the enthalpy and entropy of L-menthol fusion are

$$\Delta_{fus}H^{\circ}_{m} = (13.47 \pm 0.06)\ \ \text{J}\times\text{mol}^{-1}\times\text{K}^{-1}\ \text{and}$$
$$\Delta_{fus}S^{\circ}_{m} = (42.68 \pm 0.19)\ \ \text{J}\times\text{mol}^{-1}\times\text{K}^{-1}.$$

Table 2 lists the smoothed heat capacity values and standard thermodynamic functions of L-menthol in the condensed state in the range of 5–370 K. These values are also shown in Figs. 3–6.

The enthalpy of menthol formation in the gaseous state was calculated using the isodesmic reactions method (reactions in which the same number of same type bonds is preserved pre- and post-reaction). Menthol is a nonrigid molecule with a relatively large number of tops; therefore, the starting reagents have

Table 2. Standard thermodynamic functions of L-menthol in the temperature range of 5–370 K

***T*, K**	$C^\circ_{p,\mathrm{m}}$	$\Delta_0^T H^\circ_\mathrm{m}/T$	$\Delta_0^T S^\circ_\mathrm{m}$	$-\Delta_0^T G^\circ_\mathrm{m}/T$
	J×mol^{-1}×K^{-1}			
Crystal				
5	0.858±0.017	0.2148±0.0043	0.2864±0.0057	0.0716±0.0014
25	27.36±0.30	10.49±0.15	15.64±0.23	5.151±0.073
50	53.14±0.21	25.84±0.19	43.18±0.40	17.34±0.14
100	95.95±0.38	50.28±0.24	93.27±0.60	42.98±0.24
150	134.0±0.5	72.00±0.32	139.5±0.8	67.55±0.34
200	169.3±0.7	91.90±0.39	182.9±1.0	91.02±0.43
250	206.5±0.8	111.0±0.5	224.6±1.1	113.6±0.5
298.15	250.1±1.0	129.8±0.5	264.6±1.3	134.7±0.6
300	252.3±1.0	130.6±0.5	266.1±1.3	135.5±0.6
315.60	272.3±1.1	137.1±0.6	279.4±1.3	142.3±0.6
Liquid				
315.60	376.1±1.5	179.8±0.7	322.1±1.5	142.3±0.6
350	422.3±1.7	201.5±0.8	363.5±1.7	162.0±0.7
370	437.0±1.7	213.9±0.9	387.5±1.8	173.6±0.8

a sufficient number of rotational degrees of freedom in the gas phase isodesmic reactions.

Table 3 lists the experimental values of the formation enthalpies of the participants of the isodesmic reactions, the electronic energy of molecules, the corrections for zero-point vibrations, and temperature correction.

Table 4 shows the values for the standard enthalpies of isodesmic reactions and the corresponding standard enthalpies of gaseous L-menthol formation.

The enthalpy of menthol formation calculated using the Gaussian 4 composite quantum chemical method agreed well with the experimental value. The good correlation between the calculated and experimental values was attributed to the proper selection of the group of isodesmic reactions, which consider the internal rotation energy of the menthol molecule owing to the inclusion of alkanes (general formula C_nH_{2n+2}; with a large number of spinning tops) in the isodesmic reactions. The calculations can be considered chemically accurate because the deviation from the experimental value does not exceed 4 kJ×mol^{-1}.

The geometry optimization of the L-menthol molecule was performed as part of the calculations of its formation enthalpy in the gaseous state using the Gaussian 4 method. Fiure 7 shows the optimized structure of the most stable L-menthol conformer.

The extended Politzer equation, which includes a measure of local polarity, has the following form [16]:

$$\Delta_\mathrm{sub}H = a(SA)^2 + b\sqrt{\sigma^2_{tot}\nu} + c\prod + d\,, \tag{2}$$

where *SA* is the molecular surface area; *ν* is the measure of the balance between positive and negative extremes on the surface of the molecule; σ^2_{tot} is the measure of the potential variability on the molecular surface; and Π is the measure of local polarity.

The coefficients *a, b, c*, and *d* are selected by minimizing the deviations from the set of experimental values of sublimation enthalpies. The following coefficients were obtained previously [16]: *a* = 0.0002606 kcal×mol^{-1}×A^{-4}; *b* = 1.8247560; *c* = 0.3475950; and *d* = −0.8151050 kcal×mol^{-1}.

The molecular parameters of L-menthol and its sublimation enthalpy, which was determined according to equation (2), are given in Table 5. The error in the calculated value of the sublimation enthalpy is taken as 3%. Moreover, the confidence intervals of the calculated and recommended [7] values of L-menthol sublimation enthalpy overlap with each other, which indicates the method's reliability.

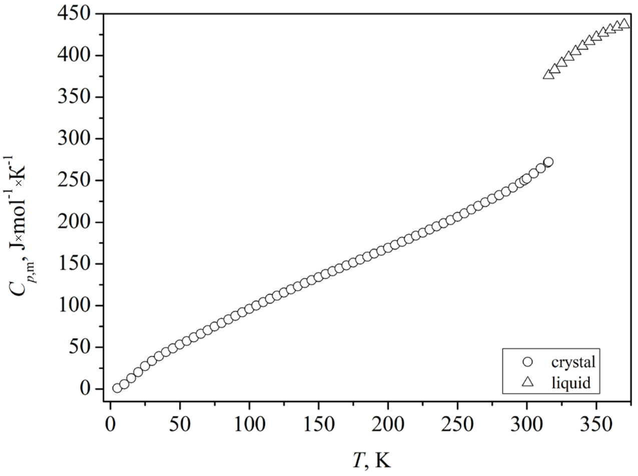

Fig. 3. Dependence of the smoothed heat capacity of L-menthol on temperature.

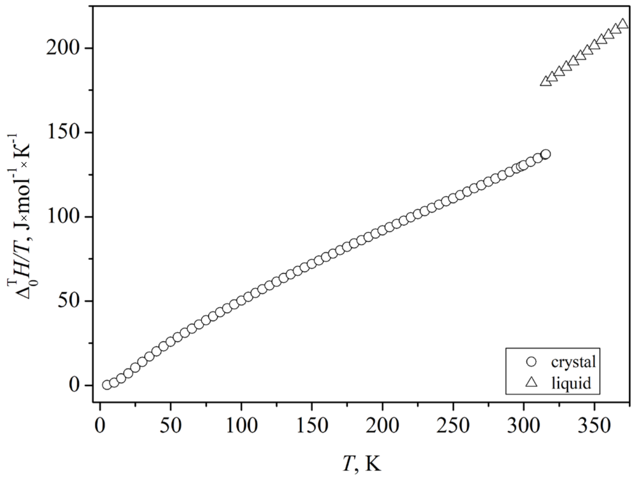

Fig. 4. Dependence of the specific enthalpy of L-menthol on temperature.

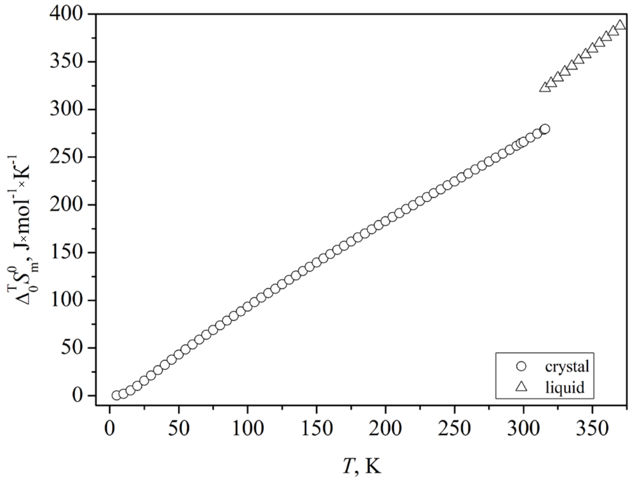

Fig. 5. Dependence of the entropy of L-menthol on temperature.

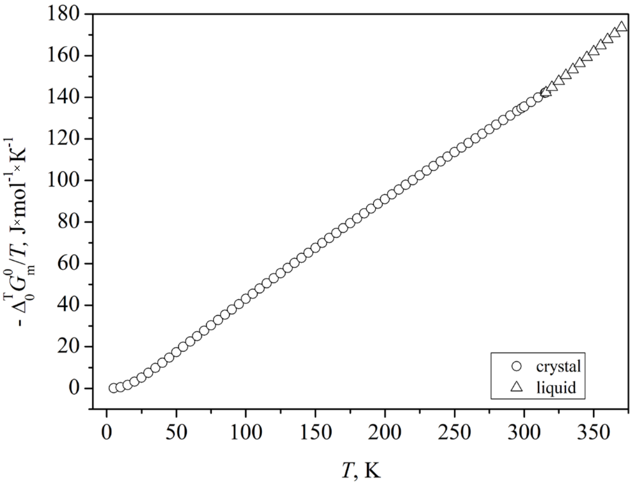

Fig. 6. Dependence of the specific Gibbs energy of L-menthol on temperature.

Table 3. Data for calculating the enthalpy of formation of L-menthol in a gaseous state using isodesmic reactions

	Compound	$\Delta_f H^\circ_{298,exp}$, kJ×mol^{-1}	E_e, hartree	ZPVE*, hartree	ΔH_0^{298}, kJ×mol^{-1}
a	Methane	–(74.6±0.3) [9]	–40.50941 [10]	0.044115	10.018
b	3-Methyl-1-butanol	–(301.3±1.5) [11]	–272.93124	0.162327	23.904
c	2-Butanol	–(293.0±1.5) [12]	–233.63117	0.134104	20.533
d	Ethane	–(84.0±0.4) [9]	–79.81155	0.073442	11.677
e	1-Propanol	–(257.3±0.4) [11]	–194.31848	0.106664	17.252
f	Isobutane	–(134.3±0.6) [13]	–158.42628 [10]	0.129264	11.672

Table 3. Continued

	Compound	$\Delta_f H^\circ_{298,exp}$, kJ×mol^{-1}	E_e, hartree	ZPVE*, hartree	ΔH_0^{298}, kJ×mol^{-1}
g	2,3-Dimethylbutane	–(177.8±1.0) [12]	–237.038739	0.184983	24.679
h	Cyclopentane	–(77.24±0.75) [15]	–196.51630 [10]	0.138268	16.273
i	2-Methylheptane	–(215.5±1.3) [14]	–315.65058	0.241232	31.942
j	2,3-Dimethylpentane	–(199.2±1.3) [14]	–276.34322	0.213000	28.451
k	Ethanol	–(234.7±0.3) [11]	–155.01281	0.078591	13.879
l	2-Methylbutane	–(154.5±0.84) [14]	–197.73172	0.157301	21.210
m	2-Methylhexane	–(195.0±1.3) [14]	–276.34430	0.213253	28.367
n	(-)-Menthol	–(393.4±2.5)	–468.26965	0.282084	35.712

* values are subject to scaling, *SF* = 0.9854.

Table 4. Standard enthalpies of isodesmic reactions and standard enthalpies of formation of L-menthol in a gaseous state

	Isodesmic reaction	$\Delta_r H^\circ_{298,exp}$, kJ×mol^{-1}	$\Delta_f H^\circ_{298}$, kJ×mol^{-1}
1	h + f + e = n + 2a	–71.6	–(391.2±1.2)
2	b + g + d = n + 3a	–54.0	–(393.3±2.1)
3	h + b + d = n + 2a	–83.0	–(396.4±1.8)
4	b + j = n + 2a	–46.5	–(397.8±2.1)
5	c + j + d = n + 3a	–42.3	–(394.7±2.2)
6	b + i = n + d + a	–31.8	–(390.0±2.0)
7	l + g + k = n + 3a	–49.3	–(392.5±1.6)
8	m + b = n + 2a	–44.3	–(391.4±2.1)

$$\left\langle \Delta_f H^\circ_{298} \right\rangle = -(393.4\pm1.9)\ \text{kJ×mol}^{-1}$$

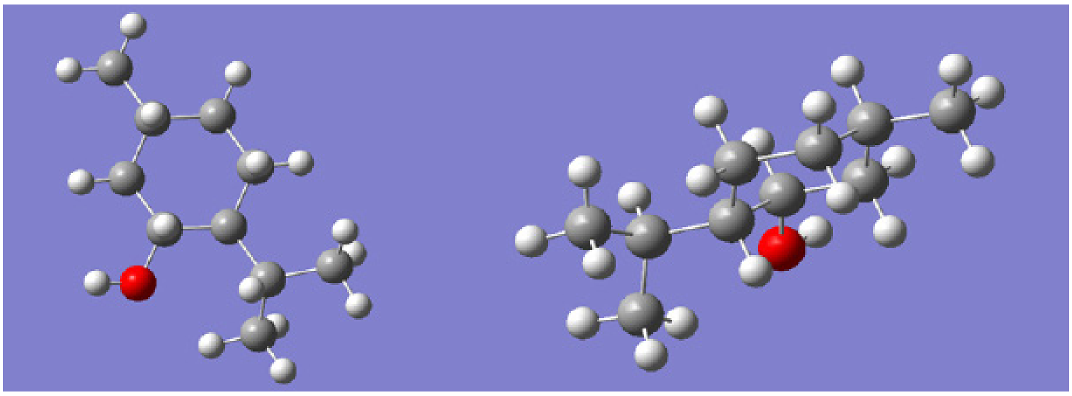

Fig. 7. Structure of the most stable conformer of L-menthol (DFT, B3LYP, 6-311G (2df, p)).

Table 5. Molecular parameters and enthalpy of sublimation of L-menthol calculated using the Politzer equation

SA, A^2	$\sigma_{tot}^2 \times \nu \left(\mathbf{kcal \times mol^{-1}}\right)^2$	П, kcal×mol^{-1}	$\Delta_{sub}H$, kcal×mol^{-1}	$\Delta_{sub}H$, kJ×mol^{-1}	$\Delta_{sub}H$(exp), kJ×mol^{-1}
214.6	17.05	5.510	20.6±0.6	86.3±2.6	84.4±1.7

CONCLUSIONS

The standard combustion energy of crystalline L-menthol was determined using combustion bomb calorimetry, based on which the standard formation enthalpies in crystalline and gaseous states were calculated. L-menthol heat capacities in the temperature range of 5–370 K and the thermodynamic parameters of its melting were determined using the low-temperature adiabatic calorimetry method. The standard thermodynamic functions (reduced enthalpy, entropy, and reduced Gibbs energy) of L-menthol in the crystalline and liquid states were calculated. Moreover, geometry optimization and calculations of the frequencies of normal modes, electronic energy, and zero-point vibration correction for the L-menthol molecule were performed using the Gaussian 4 composite quantum chemical method and GAUSSIAN 09 program. Moreover, the formation enthalpy in the gaseous state was obtained using isodesmic reactions. The sublimation enthalpy was calculated according to the electrostatic potential model using the Multiwfn 3.7 package. Finally, the calculated values of the formation enthalpy of the gaseous substance and the sublimation enthalpy of L-menthol were consistent with the experimental values (within error limits), thus confirming the reliability of the semiempirical methods that were used to determine the thermodynamic parameters of organic substances.

The authors declare no conflicts of interest.

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Submitted: November 27, 2019; Reviewed: December 03, 2019; Accepted: February 04, 2020.

Translated from Russian into English by Crimson Interactive Inc. (Enago) Corporation