



Thermodynamic properties of 2-methylfuran

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ABSTRACT

The heat capacity of 2-methylfuran in the temperature range of 8–350 K was determined by vacuum adiabatic calorimetry. The temperature, the enthalpy and the entropy of fusion and purity of investigated sample were determined by fractional melting. The smoothed thermodynamic functions (changes in enthalpy, entropy and Gibbs energy) in the region of 8–350 K were calculated. The entropies of formation and Gibbs energies of formation of 2-methylfuran at 298.15 K in the liquid and ideal gas states were found, using the literature data.

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1. Introduction

Processing of plant biomass is a promising direction in obtaining various organic substances and materials, since biomass is a renewable raw material, in contrast to fossil raw materials such as gas, oil, and coal [1]. The important products in the processing of biomass are heterocyclic compounds such as furan and its derivatives [2].

These compounds are widely used in a number of industries as solvents, polymeric materials, varnishes, dyes. They are also used as fuels and various fuel additives (to improve the operational properties of the latter). According to the literature data, 2-methylfuran has the highest results in the ability to increase the detonation resistance of gasoline [3–6]. Recent works have revealed the need for further study of the mechanism of atmospheric oxidation of 2-methylfuran and importance for obtaining reliable physicochemical properties of this compound [3–5].

A considerable experimental material on the physical and chemical properties of 2-methylfuran has been accumulated in the literature, but many characteristics are very contradictory [7]. The data on the heat capacity and melting characteristics [8–10] require clarification, since samples of low purity were studied.

This manuscript is devoted to the experimental determination of the low-temperature heat capacity and parameters of fusion of 2-methylfuran.

2. Experimental

2.1. Sample

A commercial sample of 2-methylfuran (2-MF, C₅H₆O, CAS: 534-22-5) was obtained from T.C.I. Company. According to the certificate, the sample had a purity of 98 wt%, therefore before the study it was purified. The substance (~500 ml) was purified by rectification at atmospheric pressure on a column 100 cm high with a reflux ratio of 25–30 units. To obtain a sample of optimal purity, rectification was performed continuously for 12 h. The distillate was dried over calcium chloride, and then passed through a layer of silica gel (25 ml) with particles 0.5–0.25 mm in diameter. All experimental operations were carried out in an atmosphere of dry inert gas. After cleaning, the sample had a purity of 99.95 wt % according to g.l.c. analysis. Provenance and purity of 2-methylfuran are listed in Table 1.

2.2. Adiabatic calorimetry

The heat capacity of the 2-methylfuran was measured with the help of an automated vacuum adiabatic calorimeter. Detailed description of the device configuration and calorimetric technique were done in [11,12].

The calorimetric cell consists of a cylinder titanium container (V ≈ 1 cm³), inserted into a copper sleeve with a heater ($R \approx 300 \Omega$), and an adiabatic shell. The temperature of the calorimeter was measured by a (rhodium + iron) resistance thermometer

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Table 1

Provenance and purity of 2-methylfuran.

Compound	Source	Initial mass fraction purity	Purification method	Method of analysis	Final fraction purity ^a
2-MF C ₅ H ₆ O	commercial	0.98	rectification, dried over CaCl ₂ , passed through a layer of silica gel.	g.l.c. fractional melting	0.9995 mass 0.99937 mol

^a The standard uncertainty, u , is $u(\text{g.l.c.}) = 0.0002$ mass fractions; the standard uncertainty is $u(\text{fractional melting}) = 0.00003$ mol fractions.

($R_{273.1} \sim 51 \Omega$), which was calibrated in ITS-90 [13] over the temperature range from (5 to 350) K. The temperature difference between the container and adiabatic shell was measured by an eleven-junction (copper + 0.1 wt% iron) – Chromel differential thermocouple. The adiabatic performance of the calorimeter was maintained by digital control using the computer-measuring system with an accuracy of $\pm 3 \cdot 10^{-3}$ K. High vacuum inside the calorimetric cell was kept by means of cryosorption provided with an efficient charcoal getter.

The heat capacity of the substance was measured in the process of heating the sample. Each calorimetric experiment consists of six periods. In the first period the calorimeter cell is heated to a desired temperature. A steady temperature equilibration is attained in the second period. In the third period, the temperature flow is measured, i.e. the calorimeter temperature is monitored during a selected time period to get information about rate of the temperature drift. During the fourth period, electrical energy, Q , is supplied to the calorimeter. After that, the fifth period coincides with the second, the sixth is similar to the third. The beginning temperature, T_{begin} , and the finish temperature, T_{fin} , of heating a calorimetric cell with a substance in the experiment is estimated by means extrapolate to the middle of the fourth period of the temperature drifts which were measured in the third and sixth periods. The heat capacity is found as $C = Q / (T_{\text{fin}} - T_{\text{begin}})$ at $T = (T_{\text{fin}} + T_{\text{begin}}) / 2$. The heat capacity measurement is carried out automatically by special program of PC, which includes initial adjusting of some parameters of process in a dialogue mode. When the first determination is done, the program routinely carries out the subsequent measurements.

The calorimeter was tested with a high-pure Cu (0.99995 mass fraction) and chromatographically pure *n*-heptane. Average deviations of the experimental data from the precision literature data [14,15] were 0.02 in temperature range from (7 to 20) K, 0.01 from (20 to 40) K, 0.004 from (40 to 80) K, 0.002 from (80 to 300) and 0.01 above 300 K. The obtained average deviations are experimental uncertainties of the device for determining the heat capacity. The uncertainty of the container temperature determination was estimated $\pm 2 \cdot 10^{-2}$ K within the whole range of temperatures (7–350 K).

2.3. Heat capacity

The heat capacity, $C_{p,m}/(\text{J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})$, of 2-methylfuran was measured in the temperature range from 8.14 K to 353.51 K with the temperature step $\Delta T = (T_f - T_{\text{in}}) \sim (1.0 - 1.5)$ K using liquid nitrogen and liquid helium as refrigerants. The measurements were performed at $p_{298}(\text{He})/k\text{Pa} = (10 \pm 2)$ in the container with the sample (gaseous helium was as the thermal exchange gas). The mass of the sample (reduced to vacuum) was equal to 0.72157 g. The density of 2-MF, $\rho(298.15 \text{ K}) = 0.90779 \text{ g} \cdot \text{cm}^{-3}$, was taken from [16]. The mass of the sample was determined with a precision of $\pm 5 \cdot 10^{-2}$ mg on a Mettler balance (Type 100 A5M, Max. Bel. 100 g.).

The sample of 2-MF was cooled from room temperature to liquid helium temperature at the rate $\sim (1 \text{ to } 8) \cdot 10^{-3} \text{ K} \cdot \text{s}^{-1}$. The formation of a metastable phase during cooling of the 2-MF sample was not observed.

A phase transition (melting) was detected on the heat capacity curve (Fig. 1).

The reproducibility of the heat capacity curve is 0.03–0.2%. The obtained experimental values of the heat capacity are tabulated in Table S1 (Supported data).

2.4. Melting of the sample

The triple-point temperature, T_{tp} , and the mole fraction of impurities, N_2 , of the 2-MF sample were determined by the calorimetric method of the fractional melting study [17,18]. Three experiments on the fractional melting of the sample were conducted (Fig. 2 and Table S2, Supported data). They showed a linear dependence of the equilibrium temperature of fusion, T_i , on the reciprocal fraction of the sample melted, $1/F_i$:

$$T_i/K = [(T_1/K) - (T_{\text{tp}})/K](1/F_i) + (T_{\text{tp}}/K). \quad (1)$$

here, $T_{\text{tp}} = 184.36_3 \text{ K}$ is the triple-point temperature of the pure sample, $(T_1 - T_{\text{tp}}) = -0.020 \text{ K}$ is a depression of the T_{tp} value; T_1 denotes the triple-point temperature of the completely melted sample ($F_i = 1$). Linear regression coefficient equals $r^2 = 0.995$.

The enthalpy of fusion, $\Delta_{\text{cr}}^{\text{l}}H_m^{\circ}(T_{\text{tp}})$, of 2-MF was determined calorimetrically basing on the total enthalpy absorbed during the fusion of the sample with corrections for hypothetical normal heat capacities of the crystal and liquid which the substance could have in the fusion region. The $\Delta_{\text{cr}}^{\text{l}}H_m^{\circ}(T_{\text{tp}})$ value was calculated from the equation:

$$\Delta_{\text{cr}}^{\text{l}}H_m^{\circ}(T_{\text{tp}})/(\text{J} \cdot \text{mol}^{-1}) = \Delta_{\text{tot}}H - \Delta_{T_{\text{in}}}^{T_{\text{tp}}}H_m(\text{cr}) - \Delta_{T_{\text{tp}}}^{T_f}H_m(\text{l}) - \Delta_{T_{\text{in}}}^{T_f}H_{\text{emp}} \quad (2)$$

where $\Delta_{\text{tot}}H$ is the total enthalpy absorbed during heating the sample from initial temperature T_{in} to final temperature T_f (T_{in} and T_f lay outside the pre-melting region); $\Delta_{T_{\text{in}}}^{T_{\text{tp}}}H_m(\text{cr}) = \int_{T_{\text{in}}}^{T_{\text{tp}}} C_{p,m}(\text{cr})dT$ and $\Delta_{T_{\text{tp}}}^{T_f}H_m(\text{l}) = \int_{T_{\text{tp}}}^{T_f} C_{p,m}(\text{l})dT$ are the heating enthalpies calculated by

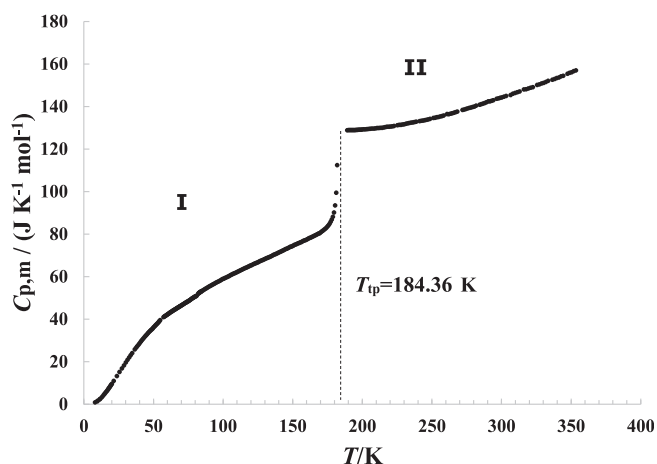


Fig. 1. Experimental molar heat capacity of crystal (I) and liquid (II) of 2-methylfuran, $C_{p,m}$, vs. temperature, T .

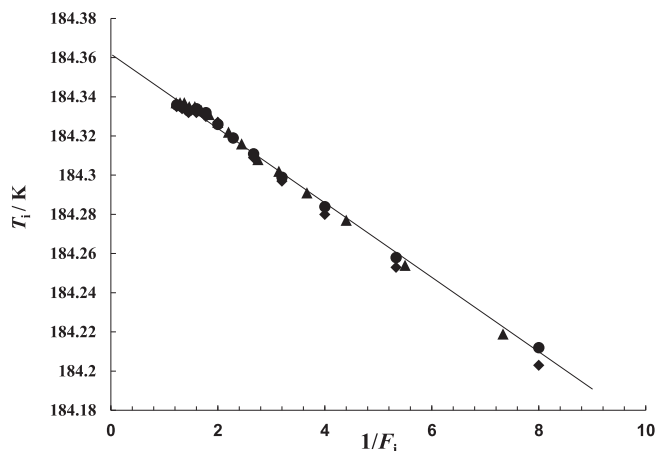


Fig. 2. The dependence of the equilibrium temperature of fusion, T_f , on the reciprocal fraction of sample melted, $1/F_i$, for three experiments.

extrapolating to T_{tp} based on the experimental values of the heat capacities of the crystal (165.31–172.55 K) and liquid (190.98–196.65 K) obtained outside the pre-melting region; $\Delta_{T_{in}}^{T_f} H_{emp}$ is enthalpy of heating of an empty container from T_{in} to T_f . The enthalpy of fusion of 2-MF (Table 2) was determined in five independent experiments.

The mole fraction of impurities, N_2 , was calculated from the formula [17]:

$$N_2 = \{(\Delta_{cr}^1 H_m^0(T_{tp})/J \cdot \text{mol}^{-1}) \cdot [(T_1/K) - (T_{tp}/K)]\} / [R \cdot (T_{tp}/K)^2], \quad (3)$$

where $R = 8.314462618 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and $\Delta_{cr}^1 H_m^0(T_{tp})$ is the enthalpy of fusion of 2-MF.

The mole fraction of impurities, N_2 , is 0.00063; relative standard uncertainty u_r is $u_r(N_2) = 0.00003$.

2.5. Approximation of heat capacity data and thermodynamic functions

The experimental values of the heat capacities were divided into temperature intervals and smoothed by polynomials of the following form:

$$C_{p,m}/(J \cdot K^{-1} \cdot \text{mol}^{-1}) = \sum_{i=0} A_i \cdot (T/K)^i, \quad (4)$$

Table 2

Molar enthalpy, $\Delta_{cr}^1 H_m^0(T_{tp})$, and entropy, $\Delta_{cr}^1 S_m^0(T_{tp})$, of fusion of 2-MF. (T_{in} and T_f is initial and final temperatures, $\Delta_{tot} H$ is the energy required to heat 1 mol of substance from T_{in} to T_f , $\Delta_{T_{in}}^{T_{tp}} H_m(cr)$ is the energy required to heat 1 mol of undisturbed crystalline phase of substance from T_{in} to T_{tp} , $\Delta_{T_{tp}}^{T_f} H_m(l)$ is the energy required to heat 1 mol of undisturbed liquid phase of substance from T_{tp} to T_f , $\Delta_{T_{in}}^{T_f} H_{emp}$ is the energy required to heat empty container T_{in} to T_f per 1 mol substance). (Molar Mass = $82.100 \text{ g} \cdot \text{mol}^{-1}$, $m_{vacuum} = 0.72157 \text{ g}$, $T_{tp} = 184.363 \text{ K}$).^a

T_{in}^b	T_f^b	$\Delta_{tot} H^c$	$\Delta_{T_{in}}^{T_{tp}} H_m(cr)^a$	$\Delta_{T_{tp}}^{T_f} H_m(l)^a$	$\Delta_{T_{in}}^{T_f} H_{emp}$	$\Delta_{cr}^1 H_m^0(T_{tp})$	$\Delta_{cr}^1 S_m^0(T_{tp})$
K		$\text{J} \cdot \text{mol}^{-1}$					$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
171.063	189.720	13197	1115	690	2374	9018	48.92
169.733	190.468	13664	1223	787	2637	9017	48.91
166.726	189.290	13976	1464	635	2856	9021	48.93
166.583	189.767	14128	1475	697	2934	9022	48.94
169.430	192.616	14282	1247	1064	2955	9016	48.90
Mean 9019 ^d						9016	48.92 ^d

^a The molar masses of the compound was calculated using relative atomic masses recommended by IUPAC [19]; standard uncertainties u are $u(\text{Molar Mass}) = 0.002 \text{ g} \cdot \text{mol}^{-1}$; $u(m_{vacuum}) = 5 \cdot 10^{-5} \text{ g}$; combined expanded uncertainty U_c is $U_c(T_{tp}) = 0.035 \text{ K}$.

^b Standard uncertainty $u(T) = 0.02 \text{ K}$.

^c Standard uncertainty $u(\Delta_{tot} H) = 28 \text{ J} \cdot \text{mol}^{-1}$.

^d Combined expanded uncertainties U_c are $U_c(\Delta_{T_{in}}^{T_{tp}} H_m(cr)) = 7 \text{ J} \cdot \text{mol}^{-1}$, $U_c(\Delta_{T_{tp}}^{T_f} H_m(l)) = 8 \text{ J} \cdot \text{mol}^{-1}$, $U_c(\Delta_{T_{in}}^{T_f} H_{emp}) = 5 \text{ J} \cdot \text{mol}^{-1}$, $U_c(\Delta_{cr}^1 H_m^0(T_{tp})) = 14 \text{ J} \cdot \text{mol}^{-1}$ and $U_c(\Delta_{cr}^1 S_m^0(T_{tp})) = 0.076 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (0.95 level of confidence).

where i denotes a degree of polynomial, A_i are coefficients calculated by method of the least squares (LSM). The temperature intervals, coefficients and root-mean-square deviations (RMS) between the calculated by Eq. (4) and experimental $C_{p,m}$ values are given in Table 3. All RMS lie within the limits of experimental uncertainties.

Heat capacity of 2-MF was extrapolated to $T \rightarrow 0$ by the equation:

$$C_{p,m}/(J \cdot K^{-1} \cdot \text{mol}^{-1}) = n'D[\Theta_D/(T/K)], \quad (5)$$

using Debye function D and adjusted parameters $\hat{n} = 5.645560$ and $\Theta_D = 132.847089$. The values of $\hat{n}$ and Θ_D were calculated by LSM in the temperature interval (8.14 to 12.77) K. The RMS deviation between the calculated by Eq (5) and experimental $C_{p,m}$ values lies within the limits of experimental errors of this temperature region and is 0.7%.

Temperature ranges in which values of the heat capacities were described by Eqs (4), (5) overlap. The crosslinking temperatures of adjacent polynomials, T_{cr-lin} , at which the difference between the calculated values of the heat capacities for two different polynomials is minimal over the entire overlap interval are given in Table 4.

Smoothed values of heat capacity $C_{p,m}/R$, entropy S_m^0/R , enthalpy $(H_m^0(T) - H_m^0(0))/RT$ and Gibbs energy $(G_m^0(T) - H_m^0(0))/RT$ from 10 to 350 K are calculated by integration of the dependences $C_{p,m} = f(T)$ obtained from Eqs. (4), (5) and are listed in Table 5.

Combined expanded uncertainties U_c (cover ratio, k , is 2) of thermodynamic functions (Table 5) were estimated in accordance with the law of propagation of uncertainty. The relative expanded uncertainty, u_r , of extrapolation to 0 K was taken equal to 5%. The combined expanded uncertainty of Gibbs energy was estimated as the sum of the enthalpy and entropy combined uncertainties.

3. Results and discussion

3.1. Thermodynamic properties of 2 - methylfuran from experimental data

There are two works on the experimental determination of the low-temperature heat capacity of 2-methylfuran: by the method of vacuum adiabatic calorimetry in the region of (5–310) K [9] and by the DSC method in the temperature range of (293.15–323.15) K [8]. In [9], the melting characteristics of 2-MF were also determined. A comparison of the data obtained in this work with the values available in the literature is given in the Fig. 3 and Table 6.

Table 3

Coefficients of Eq. (4) which approximate the experimental heat capacity of 2-MF.

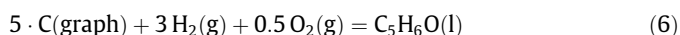
Temperature interval/ K	I	II	III	IV
	9.86–39.31	38.47–67.99	67.21–84.64	84.25–168.54
A0	6.11171191848211E + 00	3.57436029875501E + 04	–1.72886520217349E + 04	4.64182372897412E + 02
A1	–1.75932478546765E + 00	–4.85527498584665E + 03	1.15694046302043E + 03	–2.67461160206033E + 01
A2	1.79462688839923E-01	2.80343206239270E + 02	–3.08640378643913E + 01	6.20973213227383E-01
A3	–5.78189460429684E-03	–8.91565864942734E + 00	4.11113347173070E-01	–8.21583117074420E-03
A4	9.47185933958157E-05	1.68701146305178E-01	–2.73299292417675E-03	6.57057077541987E-05
A5	–6.53135831668931E-07	–1.89942944191633E-03	7.25336154160271E-06	–3.15931253058365E-07
A6		1.17842244048323E-05		8.42326367591027E-10
A7		–3.10832867690351E-08		–9.58122950276552E-13
RMS ^a	0.021238934	0.059868009	0.04941018	0.042468016
RMS,%	0.17	0.16	0.10	0.06
Temperature interval/ K	V	VI	VII	VIII
	153.18–169.34	189.23–197.47	190.17–246.25	242.56–353.51
A0	2.75040975671658E + 01	1.23647332997332E + 02	6.78462617938771E + 03	6.11019846723630E + 02
A1	3.11061324443935E-01	2.68980883143704E-02	–1.57617254835793E + 02	–6.00537661237139E + 00
A2			1.49223650302042E + 00	2.44177303230394E-02
A3			–7.06001856720378E-03	–2.55910210138365E-05
A4			1.66863268704319E-05	–4.98490426832518E-08
A5			–1.57484033768755E-08	9.53335373127007E-11
RMSa	0.061017453	0.029230206	0.04316149	0.058086885
RMS,%	0.08	0.02	0.03	0.04

^a RMS are the root-mean-square deviations between the calculated by Eq. (4) and experimental $C_{p,m}$ values.**Table 4**Cross-linking temperatures of two adjacent polynomials, T_{cr-lin} .

Temperature intervals/ K	T_{cr-lin}/ K
8.14–12.77 and 9.86–39.31	11.51
9.86–39.31 and 38.47–67.99	39.31
38.47–67.99 and 67.21–84.64	67.60
67.21–84.64 and 84.25–168.54	84.64
84.25–168.54 and 153.18–169.34	166.93
153.18–169.34 and 189.23–197.47	–
189.23–197.47 and 190.17–246.25	194.22
190.17–246.25 and 242.56–353.51	243.79

The heat capacities of the liquid 2-MF obtained in this paper and in [8] differ by 3.8% (Fig. 3 and Table 6). The values of the heat capacities of liquid 2-MF in this work and in [9] are in good agreement, whereas the discrepancies from 0.4 to 7.7% are observed in the region of the solid phase (Fig. 3). The melting characteristics obtained in this work differ from [9] (Table 6): T_{tp} by 2.46 K; $\Delta_{cr}^l H_m^0(T_{tp})$ by 0.467 kJ · mol^{–1} (5%). The process of crystallization of 2-MF by the method of Time-resistance cooling curves was studied in [10]. The authors noted that slow cooling (cooling rate not specified) produces a metastable crystalline phase of 2-methylfuran (melting at $T = 171.23$ K) and a crystalline phase (with melting at $T = 182.96$ K). The purity of the test sample was 99.5%. In [9] the metastable phase was not found during an intensive search for it within the variation of cooling parameters possible in the cryostat. We also did not find the formation of a metastable phase at different cooling rates of 2-MF (from 0.03 to 0.008 K · s^{–1}). The discrepancies of the experimental values of heat capacity and melting characteristics with those obtained in [8–10] can be explained by the presence of a large number of unidentified impurities in the samples of 2-MF and a considerable error of the DSC method.

The calculation of standard entropy of formation of liquid 2-methylfuran, $\Delta_f S_m^0(l)$, at 298.15 K (Table 7) was conducted on the basis of the absolute entropies of 2-MF, $S_m^0(298.15)$ (Table 5), C(graph.), H₂(g), and O₂(g) [20] according to the reaction:



The Gibbs energy of formation of liquid 2-MF at 298.15 K (Table 7) was found, using the obtained value of the entropy of formation, $\Delta_f S_m^0(l)$, and literature data on the enthalpy of formation, $\Delta_f H_m^0(l)$, obtained for a high-purity sample of 2-MF (99.974%) [21].

The thermodynamic functions of 2-MF in the ideal gas state at 298.15 K, $\Delta_f S_m^0(g)$ and $\Delta_f C_m^0(g)$ (Table 7), were calculated on the basis of the corresponding value of entropy, $S_m^0(T)$, in the condensed state (Table 5) and literature data on enthalpy of vaporization, $\Delta_f^g H_m^0$, and the enthalpy of formation, $\Delta_f H_m^0(g)$ [21]. The entropy of compression of the ideal gas from $p(298.15 \text{ K}) = 23.094 \text{ kPa}$ to 101.325 kPa, $\Delta S_{comp} = R \cdot \ln\{p(298.15)/101.325 \text{ kPa}\}$, was calculated using data on the saturated vapor pressure from [7].

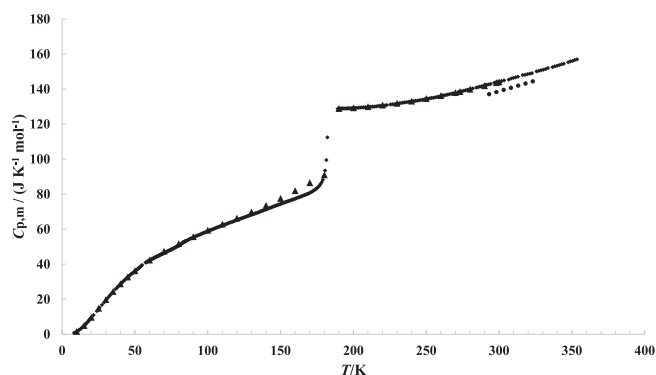
3.2. Comparison of experimental and computed gas-phase thermodynamic properties

Among the thermodynamic functions of 2-methylfuran given in Table 7 are the experimental gas-phase enthalpy of formation and entropy, whose values can be estimated with high accuracy by quantum chemical calculations. It is especially interesting to study these quantities because there is some discrepancy between the experimental gas-phase enthalpies of formation of furan and 2-methylfuran and values reported from previous theoretical calculations (Table 8), and because the accurate values of entropy, heat capacity, and enthalpy change for gaseous 2-methylfuran can be calculated by statistical thermodynamics using the experimental molecular parameters available from the literature. Furan is considered in this work due to its importance in the calculation of $\Delta_f H_m^0$ values of different furan derivatives.

The enthalpy of formation determined by Feller and Simmie [25] by high quality CCSD(T)-F12b/CBS method agrees well with the experimental value for furan, while the same method predicts the enthalpy of formation of 2-methylfuran to be $-80.3 \text{ kJ} \cdot \text{mol}^{-1}$, which is $4 \text{ kJ} \cdot \text{mol}^{-1}$ lower than the experimental value. The composite CBS-QB3 and CBS-APNO methods [26] in combination with 27 isodesmic reactions, on the other hand, lead to the overestimated value for furan. In our recent work [28], it was shown that for cyclic compounds, the most accurate results can be obtained when the DLPNO-CCSD(T₁)/CBS method is used in combination with different working reactions including simple reactions containing small reference species. Based on these results, the

Table 5Smoothed molar thermodynamic functions ($C_{p,m}(T)/R$, $[H_m^0(T) - H_m^0(0)]/RT$, $[G_m^0(T) - H_m^0(0)]/RT$) of 2-MF in the condensed state ($p^0 = 10^2$ kPa; $R = 8.314462618$ J·K⁻¹·mol⁻¹).^a

T / K	$C_{p,m}(T)/R$	$\Delta(C_{p,m}(T)/R)$	$[H_m^o(T) - H_m^o(0)]/RT$	$\Delta([H_m^o(T) - H_m^o(0)]/RT)$	$S_m^o(T)/R$	$\Delta(S_m^o(T)/R)$	$-[G_m^o(T) - H_m^o(0)]/RT$	$\Delta(-[G_m^o(T) - H_m^o(0)]/RT)$	
Crystal									
5	0.02345	0.00166	0.00601	0.00030	0.00798	0.00056	0.00196	0.00010	
10	0.1871	0.0085	0.0474	0.0024	0.0628	0.0031	0.01543	0.00077	
15	0.588	0.014	0.1544	0.0047	0.2067	0.0068	0.0523	0.0026	
20	1.145	0.024	0.3305	0.0081	0.450	0.012	0.1194	0.0060	
25	1.753	0.019	0.5539	0.0096	0.770	0.015	0.217	0.011	
30	2.356	0.025	0.804	0.012	1.144	0.019	0.339	0.017	
35	2.924	0.030	1.067	0.014	1.550	0.024	0.483	0.024	
40	3.420	0.026	1.331	0.016	1.974	0.028	0.643	0.032	
45	3.894	0.027	1.591	0.017	2.405	0.031	0.815	0.048	
50	4.293	0.028	1.841	0.018	2.836	0.033	0.995	0.051	
55	4.730	0.029	2.083	0.019	3.265	0.036	1.182	0.055	
60	5.095	0.030	2.320	0.020	3.694	0.039	1.374	0.058	
65	5.355	0.030	2.544	0.020	4.112	0.041	1.568	0.061	
70	5.633	0.029	2.755	0.021	4.519	0.043	1.764	0.064	
75	5.902	0.030	2.955	0.022	4.917	0.045	1.961	0.067	
80	6.158	0.026	3.148	0.022	5.306	0.047	2.158	0.069	
90	6.639	0.026	3.509	0.022	6.059	0.050	2.550	0.072	
100	7.067	0.027	3.844	0.023	6.781	0.053	2.937	0.075	
110	7.456	0.028	4.155	0.023	7.473	0.055	3.319	0.078	
120	7.827	0.029	4.445	0.024	8.138	0.058	3.693	0.081	
130	8.191	0.030	4.719	0.024	8.779	0.060	4.059	0.084	
140	8.556	0.031	4.980	0.024	9.399	0.062	4.419	0.087	
150	8.924	0.032	5.231	0.025	10.002	0.064	4.771	0.089	
160	9.294	0.033	5.474	0.025	10.590	0.067	5.116	0.092	
170	9.670	0.034	5.709	0.026	11.165	0.069	5.455	0.094	
180		10.088	0.035	5.941	0.026	11.729	0.071	5.788	0.097
184.36		10.307	0.035	6.041	0.027	11.973	0.071	5.932	0.098
Liquid									
184.36		15.480	0.051	11.925	0.037	17.856	0.082	5.93	0.12
190		15.485	0.051	12.030	0.037	18.323	0.084	6.29	0.12
200		15.530	0.051	12.204	0.038	19.118	0.086	6.91	0.12
210		15.603	0.051	12.364	0.039	19.878	0.089	7.51	0.13
220		15.704	0.052	12.514	0.039	20.606	0.091	8.09	0.13
230		15.839	0.052	12.655	0.040	21.307	0.093	8.65	0.13
240		15.993	0.052	12.791	0.040	21.984	0.096	9.19	0.14
250		16.15	0.16	12.922	0.045	22.64	0.10	9.72	0.15
260		16.35	0.16	13.050	0.050	23.28	0.11	10.23	0.16
270		16.57	0.17	13.176	0.054	23.90	0.11	10.72	0.17
280		16.81	0.17	13.302	0.058	24.51	0.12	11.20	0.18
290		17.06	0.17	13.427	0.062	25.10	0.13	11.67	0.19
298.15		17.26	0.17	13.529	0.065	25.58	0.13	12.05	0.20
300		17.31	0.17	13.552	0.065	25.68	0.13	12.13	0.20
310		17.57	0.18	13.678	0.069	26.25	0.14	12.58	0.21
320		17.84	0.18	13.803	0.072	26.82	0.14	13.01	0.22
330		18.11	0.18	13.930	0.076	27.37	0.15	13.44	0.23
340		18.41	0.18	14.057	0.079	27.91	0.16	13.86	0.23
350		18.73	0.19	14.186	0.082	28.45	0.16	14.27	0.24

^a The standard uncertainties are $u(p^0) = 0.5$ kPa and $u(T) = 0.02$ K; combined expanded uncertainties thermodynamic functions are $\Delta(C_{p,m}(T)/R)$, $\Delta([H_m^0(T) - H_m^0(0)]/RT)$, $\Delta(S_m^0(T)/R)$, $\Delta(-[G_m^0(T) - H_m^0(0)]/RT)$ (0.95 level of confidence).**Fig. 3.** Experimental molar heat capacity, $C_{p,m}$ / (J·K⁻¹·mol⁻¹) of 2-MF: [8] - ●, [9] - ▲, this work - ◆.

DLPNO-CCSD(T_1) method [29] was used in the present work to calculate the enthalpies of formation. The ORCA 4.2.1 program release [30] was employed for the DLPNO calculations, including the extrapolation procedure [31] implemented in the ORCA. The geometry optimization at the B3LYP-D3(BJ)/def2-TZVPP level was performed using the Gaussian 16 suite of programs [32].

The enthalpies of formation of furan, 2- and 3-methylfuran calculated by DLPNO-CCSD(T_1)/CBS method using isogyric, isodesmic, and homodesmotic reactions are given in Table S3 of Supplementary data. As seen from this table, all reactions reproduce the experimental enthalpies of formation of furan and 2-methylfuran within 2.5 kJ·mol⁻¹, thus confirming the accuracy of experimental values [21,22]. A good agreement between theory and experiment show not only the reactions with furan derivatives, but also the reactions with small reference molecules.

The thermodynamic functions $\{S_m^0(g)(T)$, $C_{p,m}(g)(T)$, $[H_m^0(T) - H_m^0(0)](g)$ and $[G_m^0(T) - H_m^0(0)]/T(g)\}$ of 2-methylfuran were calcu-

Table 6Thermodynamic characteristics of the 2-methylfuran, heat capacity, $C_{p,m}(298.15)$, triple-point temperature, T_{tp} , enthalpy, $\Delta_{cr}^L H_m^0(T_{tp})$, and entropy, $\Delta_{cr}^L S_m^0(T_{tp})$.

Ref	Purity	Method of analysis	$C_{p,m}(298.15) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T_{tp} / K	$\Delta_{cr}^L H_m^0(T_{tp}) / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{cr}^L S_m^0(T_{tp}) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
[9]	99.16 (mol. %)	fractional melting	143.72 ± 0.14	181.90 ± 0.02	8.552	47.01
[8]	99 (wt. %)	certificate of Sigma-Aldrich	138.325 ± 0.002	–	–	–
[10]	99.5%	synthesized and purified by distillation.	–	182.96 ± 0.01	–	–
this work ^a	99.95 $\pm$ 0.02 (wt. %) 99.937 $\pm$ 0.003 (mol. %)	g.l.c. fractional melting	143.51 ± 0.29	$184.36_3 \pm 0.03_5$	9.019 ± 0.014	48.92 ± 0.076

^a Uncertainties thermodynamic characteristics are combined expanded uncertainties (0.95 level of confidence).**Table 7**Thermodynamic functions formation in liquid ($\Delta_f S_m^0(l)$, $\Delta_f H_m^0(l)$, $\Delta_f G_m^0(l)$) and gas ($\Delta_f S_m^0(g)$, $\Delta_f H_m^0(g)$, $\Delta_f G_m^0(g)$) states, enthalpy of vaporization, $\Delta_v H_m^0$, and entropy of compression, ΔS_{comp} , of 2-methylfuran at 298.15 K.^a

Thermodynamic functions	Values
$\Delta_f S_m^0(l) / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	-310.7 ± 0.8
$\Delta_f H_m^0(l) / (\text{kJ}\cdot\text{mol}^{-1})$	-108.3 ± 1.1^b
$\Delta_f G_m^0(l) / (\text{kJ}\cdot\text{mol}^{-1})$	-15.7 ± 1.1
$\Delta_f H_m^0(g) / (\text{kJ}\cdot\text{mol}^{-1})$	31.9 ± 0.5^b
$\Delta_f S_m^0(g) / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	107.0 ± 1.7
$\Delta S_{comp} / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	-12.30
$S_m^0(g) / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	307.4 ± 1.8
$\Delta_f S_m^0(g) / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	-216.0 ± 1.9
$\Delta_f H_m^0(g) / (\text{kJ}\cdot\text{mol}^{-1})$	-76.4 ± 1.2^b
$\Delta_f G_m^0(g) / (\text{kJ}\cdot\text{mol}^{-1})$	-12.0 ± 1.3

^a Uncertainties thermodynamic functions are combined expanded uncertainties (0.95 level of confidence).^b Ref. [21].

lated by standard statistical thermodynamics formulas using the rigid-rotor harmonic-oscillator approximation with correction for internal rotation. The first calculation, indicated in the Table 9 as “I”, was performed using experimental molecular parameters available from the literature [33–35], whereas the computed molecular parameters were used in the second calculation, indicated as “II”. The geometric parameters and vibrational frequencies were obtained at the B3LYP-D3(BJ)/def2-TZVPP level and the barrier for internal rotation of CH_3 group was estimated using the DLPNO-CCSD(T_1)/CBS//B3LYP-D3(BJ)/def2-TZVPP model. Experimental and theoretical molecular parameters are given in Table S4 of Supplementary data. The thermodynamic properties in the temperature interval from (0 to 1500) K are listed in Tables S5–S7 and the values at 298.15 K are given in Table 9. As can be seen from Table 9, the thermodynamic properties calculated from both experimental and theoretical molecular parameters agree with the experimental values within their uncertainties.

Table 8Comparison of experimental and calculated gas-phase enthalpies of formation, $\Delta_f H_m^0(g)$, of furan, 2- and 3-methylfuran.

	Experiment $\Delta_f H_m^0(g) / \text{kJ}\cdot\text{mol}^{-1}$ Reference	Calculation $\Delta_f H_m^0(g) / \text{kJ}\cdot\text{mol}^{-1}$ Reference
Furan	-34.7 ± 0.6 [22]	-32.2 ± 2.0^a [23] -36.0^a [24] -34.8 ± 3.0^b [25] -31.4^c [26] -35.1 ± 2.7^d This work -80.8 ± 0.5^e [27] -80.3 ± 5.0^b [25] -78.7^c [26] -76.9 ± 2.6^d This work -69.5 ± 0.5^e [27] -67.4^c [26] -65.9 ± 2.6^d This work
2-Methylfuran	-76.4 ± 1.2 [21]	
3-Methylfuran		

^a CCSD(T)/CBS method.^b Feller-Petersen-Dixon method, CCSD(T)-F12b/CBS.^c CBS-QB3 and CBS-APNO methods using isodesmic work reactions.^d DLPNO-CCSD(T_1)/CBS method using isogyric, isodesmic, and homodesmotic reactions (see Table S3 of Supplementary data).^e CBS-QB3, CBS-APNO, and G3 methods using isodesmic work reactions.**Table 9**Comparison of experimental and computed gas-phase thermodynamic main functions $C_{p,m}(g)$, $[H_m^0(T) - H_m^0(0)](g)$, $S_m^0(g)$, $[G_m^0(T) - H_m^0(0)](g)$ and functions of formation, $\Delta_f S_m^0(g)$, $\Delta_f H_m^0(g)$, $\Delta_f G_m^0(g)$ of 2- and 3-methylfuran at $T = 298.15$ K.

Property	2-Methylfuran			3-Methylfuran
	Experiment ^a	Calculation I ^b	Calculation II ^c	Calculation II ^c
$\Delta_f H_m^0(g) / \text{kJ}\cdot\text{mol}^{-1}$	-76.4 ± 1.2^d	-76.4 ± 1.2	-76.9 ± 2.6	-65.9 ± 2.5
$S_m^0(g) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	307.4 ± 1.8	308.4 ± 1.5	308.9 ± 1.8	310.2 ± 1.8
$C_{p,m}(g) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		89.5 ± 1.0	89.2 ± 1.0	89.0 ± 1.0
$[H_m^0(T) - H_m^0(0)](g) / \text{kJ}\cdot\text{mol}^{-1}$		16.7 ± 0.7	16.7 ± 0.7	16.8 ± 0.7
$[G_m^0(T) - H_m^0(0)](g) / \text{kJ}\cdot\text{mol}^{-1}$		252.5 ± 1.5	252.9 ± 1.8	254.0 ± 1.8
$\Delta_f S_m^0(g) / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	-216.0 ± 1.9	-214.9 ± 1.6	-214.4 ± 1.9	-213.1 ± 1.9
$\Delta_f G_m^0(g) / \text{kJ}\cdot\text{mol}^{-1}$	-12.0 ± 1.3	-12.3 ± 1.3	-13.0 ± 2.7	-2.4 ± 2.6

^a Experimental data from Table 7.^b Calculated using experimental molecular parameters.^c Calculated using theoretical molecular parameters.^d Ref. [21].

The reliable estimates obtained for 2-methylfuran make it possible to predict with high accuracy the thermodynamic properties for 3-methylfuran for which there are no experimental data. The computed values for 3-methylfuran are given in Table 8.

4. Conclusions

For a sample of 2-methylfuran of high purity, experimental low-temperature heat capacities and melting characteristics were measured. Calculations of thermodynamic functions on the basis of experimental data and by high level quantum chemical methods are carried out. A good agreement between theory and experiment allowed us to confirm, clarify and correct the thermodynamic data available in the literature for 2-methylfuran.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jct.2021.106447>.

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