



Thermodynamic properties of L-threonine



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ABSTRACT

Standard molar enthalpy of formation in the solid state at $T = 298.15$ K of L-threonine was derived from energy of combustion determined by static bomb combustion calorimetry. Heat capacity of L-threonine was measured by vacuum adiabatic calorimetry over the temperature range (7.37–371.97) K. Heat capacities and main thermodynamic functions in solid state were tabulated as a function of temperature from 5 K to 370 K. The entropy of formation and Gibbs energy of formation at $T = 298.15$ K of L-threonine in the condensed state were computed on the basis of the experimental results obtained. All results are compared with experimental values reported in the literature.

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1. Introduction

L-threonine ($C_4H_9O_3N$, CAS: 72-19-5, L-Thr) is an essential amino acid, which plays an important role in human life. L-Thr is involved in the natural synthesis of protein and enzymes, supports normal functioning of the Central nervous, immune and cardio-vascular systems and also has other useful properties (positive effect on the gastrointestinal tract, stimulates brain activity, etc.).

The literature review showed that the experimental values of the enthalpy of formation of L-Thr [1–4] are different approximately by $30 \text{ kJ}\cdot\text{mol}^{-1}$, therefore refining of this value is desirable.

The data on heat capacity, entropy of formation and free energy of formation of L-Thr in literature are absent.

This work is a continuation of our experimental determination of thermodynamic characteristics of the essential amino acids that form the primary structure of a protein [5–7]. Knowledge of accurate thermodynamic properties of amino acids is necessary for understanding the process of protein biosynthesis.

2. Experimental

2.1. Sample

The commercial sample of L-Thr was obtained from Matrix Company. According to the certificate, the content of the basic substance was 0.993 mass fraction. The commercial sample was purified twice by recrystallization from a saturated aqueous solution (deionized water, “MilliQ”) with excess isopropanol (LiCrosolv, LC-MS grade); precipitated crystals of L-Thr were dried in vacuum (~ 2.6 Pa) and then in a desiccator over phosphorus oxide to constant weight. According to elemental analysis, found (mass%): carbon (40.2 ± 0.2), hydrogen (7.7 ± 0.3) and nitrogen (11.8 ± 0.3). This corresponds to (0.9991 ± 0.0008) mass fractions of L-Thr in the sample. Theoretical calculation gives, respectively, (mass%): 40.33, 7.62, and 11.76. The purity of the sample L-Thr further was confirmed by the CO_2 -analysis of the gaseous products of combustion (0.9999 ± 0.0002) mass fraction. Provenance and purity of L-Thr are listed in Table 1.

The molar mass of the compound (Molar Mass = $119.12 \text{ g}\cdot\text{mol}^{-1}$) was calculated on based relative atomic masses recommended in [8]. The density, ρ , of L-Thr equals $1.464 \text{ g}\cdot\text{cm}^{-3}$ at $T = 298.15$ K from [9]. Storage of the sample L-Thr and all operations with it were carried out in a stream of dry argon.

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Table 1
Provenance and purity of L-threonine.

Compound	Source	Initial mass fraction purity	Purification method	Method of analysis	Final mass fraction purity
L-Thr (C ₄ H ₉ NO ₃)	commercial	0.993	two-fold recrystallization	elemental analysis analysis of CO ₂ (g)	0.9991 0.9999

2.2. Combustion calorimetry

The energy of combustion of L-Thr was determined using a static-bomb isoperibolic calorimeter; calorimeter apparatus and the technique determining the energy of combustion were similar to that described in [5,10]. The energy equivalent of calorimeter, ε , was determined by combustion of thermochemical standard benzoic acid (K-1 brand, D.I. Mendeleev Research Institute of Metrology) with purity is 99.997 mol%. Its energy of combustion in certified conditions was $\Delta_b u = (-26432.5) \text{ J} \cdot \text{g}^{-1}$ at $T = 298.15 \text{ K}$ (combined expanded uncertainty of $\Delta_b u$ is $U_c(\Delta_b u) = 1.9 \text{ J} \cdot \text{g}^{-1}$; standard uncertainty of T is $u(T) = 0.05 \text{ K}$). Temperature rise $\sim 1 \text{ K}$ was measured by a copper resistance thermometer and a bridge scheme with sensitivity of $\sim 5 \cdot 10^{-5} \text{ K}$.

Sample L-Thr ($\sim 0.50 \text{ g}$) was pressed into tablet on a hydraulic press, sealed into a Terylene-film bag and burned with a Tablet of benzoic acid to provide a temperature rise $\sim 1 \text{ K}$.

Weighing was carried out with a precision of $\pm 2 \times 10^{-3} \text{ mg}$ on a Mettler balance (Type M58 A Max. Bel. 20 g.). At the bottom of the bomb was placed 2 mL of distilled water to dissolve the NO₂(g), formed in the experiment. The bomb was charged with purified oxygen to initial pressure 3.04 MPa; the initial temperature of the experiments was 298.15 K and does not differ from it more than $\pm 0.03 \text{ K}$. Provision for ignition was made by means of a platinum wire (diameter of 0.1 mm) heated by the discharge of a capacitor.

In the products of the combustion determined CO₂ (g) by the Rossini method [11], and controlled the absence of CO (g), using indicator tubes (TU. 12.43.20-76, sensitivity $6 \times 10^{-6} \text{ g CO}$). Traces

of soot have been found in separate experiments (№ 2, 5, 8, 9 in Table 2) and appropriate corrections were made. The results of CO₂ analysis (0.9999 ± 0.0002) mass fraction indicate the completeness of combustion of L-threonine and high purity of the investigated sample. The content of HNO₃ in the solution was determined by titration of washing waters by $\sim 0.1 \text{ mol} \cdot \text{dm}^{-3}$ of NaOH (aq). The energy of combustion of L-Thr was determined from nine combustion experiments. Calculations of the combustion energy are based on the sample masses. The specific combustion energy, $\Delta_c u^\circ$, was computed using the following formula:

$$-\Delta_c u = [(\varepsilon \Delta R_{\text{corr}} - q(\text{b.a.}) - q(\text{f}) - q(\text{HNO}_3) + q(\text{s}) - q(\text{st}))] \cdot m^{-1} \quad (1)$$

The results are shown in Table 2.

2.3. Adiabatic calorimetry

The heat capacity of the L-Thr was measured in a fully automated vacuum adiabatic calorimeter combined with a computer-measuring system (Termis, Moscow). The detailed description of the device configuration and calorimetric technique is reported in [15,16]. The calorimetric cell consists of a cylinder titanium container ($V \approx 1 \text{ cm}^3$), 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 ($R_{273.15} \approx 51 \Omega$), which was calibrated in ITS-90 [17] over the temperature range from (5 to 373) K. The temperature difference between the container and adiabatic shell was measured by

Table 2
Combustion energy of L-threonine at $T = 298.15 \text{ K}$ (Molar Mass = $119.12 \text{ g} \cdot \text{mol}^{-1}$; $\rho = 1.464 \text{ g} \cdot \text{cm}^{-3}$ [9]; $P^\circ = 101.3 \text{ kPa}$)^a.

№	m ^b /g	$\Delta R_{\text{corr}}^c/\Omega$	$\varepsilon \cdot \Delta R_{\text{corr}}^d/\text{J}$	q(b.a.) ^e /J	q(f) ^f /J	q(HNO ₃) ^g /J	q(s) ^h /J	q(st) ⁱ /J	[CO ₂] ^j	$(-\Delta_c u^\circ)^k/(\text{J} \cdot \text{g}^{-1})$
1	0.495148	0.238193	13900.0	4338.8	852.6	25.2	0	9.0	0.9997	17518.8
2	0.503027	0.242773	14167.4	4667.5	658.3	26.8	3.3	9.1	–	17512.0
3	0.517502	0.239615	13983.1	4339.6	540.0	27.9	0	8.9	–	17520.1
4	0.516141	0.239809	13979.5	4321.4	581.3	28.8	0	8.8	0.9999	17513.0
5	0.513765	0.236756	13801.5	4190.9	572.7	28.2	1.8	8.6	0.9999	17523.4
6	0.517720	0.237962	13871.8	4192.0	579.0	30.2	0	8.6	1.0001	17503.7
7	0.511489	0.232972	13580.9	4027.7	559.3	25.0	0	8.5	1.0001	17518.3
8	0.511377	0.233339	13602.3	4042.1	572.2	26.1	3.2	8.5	–	17514.7
9	0.514762	0.236535	13788.6	4167.0	577.2	25.4	9.2	8.7	0.9997	17521.7
Mean									0.9999 ^l	17516.2 ^m

^a Standard uncertainties u are $u(T) = 0.01 \text{ K}$, $u(\text{Molar Mass}) = 0.02 \text{ g} \cdot \text{mol}^{-1}$, $u(P^\circ) = 0.5 \text{ kPa}$.

^b m is mass of the sample; it was weighed with a precision of $\pm 2 \cdot 10^{-3} \text{ mg}$ on a Mettler balance (Type M58A Max. Bel. 20g.), and was reduced to a vacuum.

^c ΔR_{corr} is the increase of the thermometer resistance corrected for heat exchange; standard uncertainty u is $u(\Delta R_{\text{corr}}) = 1 \cdot 10^{-5} \Omega$.

^d $\varepsilon \cdot \Delta R_{\text{corr}}$ is the total energy evolved; where ε is the energy equivalent of the calorimeter (№ 1–3: $\varepsilon = 58260.5 \text{ J} \cdot \Omega^{-1}$, № 4–9: $\varepsilon = 58198.3 \text{ J} \cdot \Omega^{-1}$) corrected for the difference between the heat capacity of the compounds contained in the bomb after combustion of the studied compound and of benzoic acid; combined expanded uncertainties U_c are $U_c(\varepsilon)$ (№ 1–3) = $7.7 \text{ J} \cdot \Omega^{-1}$; $U_c(\varepsilon)$ (№ 4–9) = $7.5 \text{ J} \cdot \Omega^{-1}$ (0.95 level of confidence).

^e $q(\text{b.a.})$ is the correction for the energy of combustion of benzoic acid, calculated from $(-26412.0) \text{ J} \cdot \text{g}^{-1}$, which is obtained from certificate value by introducing amendment for reduction to the standard state [11]; combined expanded uncertainty U_c is $U_c(q(\text{b.a.})) = 0.3 \text{ J}$ (0.95 level of confidence).

^f $q(\text{f})$ is the correction for the energy of combustion of Terylene-film.; combined expanded uncertainty U_c is $U_c(q(\text{f})) = 0.2 \text{ J}$ (0.95 level of confidence). The energy of combustion of Terylene-film is $(-22928) \text{ J} \cdot \text{g}^{-1}$ [12].

^g $q(\text{HNO}_3)$ is the correction for the energy formation of solution HNO₃(aq) from N₂(g), O₂(g) and H₂O(l) (based on $-59.1 \text{ kJ} \cdot \text{mol}^{-1}$ the molar energy of formation of aqueous nitric acid [13,14]); combined expanded uncertainty U_c is $U_c(q(\text{HNO}_3)) = 0.002 \text{ J}$ (0.95 level of confidence).

^h $q(\text{s})$ is the correction for the presence of soot in the crucible (the energy of combustion of soot $-32763 \text{ J} \cdot \text{g}^{-1}$ is calculated from the standard enthalpy of formation of CO₂ [13]); combined expanded uncertainty U_c is $U_c(q(\text{s})) = 0.003 \text{ J}$ (0.95 level of confidence).

ⁱ $q(\text{st})$ is the correction to standard state [11]; standard uncertainty u is $u(q(\text{st})) = 0.08 \text{ J}$.

^j [CO₂] is the ratio of the mass of CO₂ determined experimentally to that calculated theoretically.

^k $(-\Delta_c u^\circ)$ is the standard specific energy of combustion.

^m The mean value $(-\Delta_c u^\circ)$, combined expanded uncertainty U_c is $U_c(-\Delta_c u^\circ) = 4.7 \text{ J} \cdot \text{g}^{-1}$ (0.95 level of confidence).

^l The mean value [CO₂], combined expanded uncertainty U_c is $U_c([\text{CO}_2]) = 2 \cdot 10^{-4}$ (0.95 level of confidence).

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