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Thermodynamic properties of vitamin B_2

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ABSTRACT

In the present work temperature dependence of heat capacity of vitamin B_2 (riboflavin) has been measured for the first time in the range from 6 to 322 K by precision adiabatic vacuum calorimetry. Based on the experimental data, the thermodynamic functions of the vitamin B_2, namely, the heat capacity, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$ and Gibbs function $G^\circ(T) - H^\circ(0)$ have been determined for the range from $T \to 0$ to 322 K. The value of the fractal dimension D in the function of multifractal generalization of Debye's theory of the heat capacity of solids was estimated and the character of heterodynamics of structure was detected. In a calorimeter with a static bomb and an isothermal shield, the energy of combustion of the riboflavin has been measured at 298.15 K. The enthalpy of combustion $\Delta_c H^\circ$ and the thermodynamic parameters $\Delta_f H^\circ$, $\Delta_f S^\circ$, $\Delta_f G^\circ$ and of reaction of formation of the riboflavin from simple substances at T = 298.15 K and p = 0.1 MPa have been calculated.

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1. Introduction

Riboflavin (PubChem CID: 493570), also known as vitamin B_2 is an easily absorbed colored micronutrient with a key role in maintaining health in humans and animals. It is the central component of the cofactors flavin adenine dinucleotide (FAD) and flavin mononucleotide (FMN), and is therefore required by all flavoproteins. The current recommended dietary allowances (RDA) for riboflavin for adult men and women are 1.3 mg/day and 1.1 mg/day, respectively [1]. Riboflavin has been used in several clinical and therapeutic situations. For over 30 years, riboflavin supplements have been used as part of the phototherapy treatment of neonatal jaundice. The light used to irradiate the infants breaks down not only bilirubin, the toxin causing the jaundice, but also the naturally occurring riboflavin within the infant's blood, so extra supplementation is necessary [2]. Various biotechnological processes have been developed for industrial scale riboflavin biosynthesis using different microorganisms, including filamentous fungi such as *Ashbya gossypii*, *Candida famata* and *Candida flaveri*, as well as the bacteria *Corynebacterium ammoniagenes* and *Bacillus subtilis* [3].

The goals of this work include calorimetric determination of the standard thermodynamic functions of the riboflavin with the purpose of describing biochemical and industrial processes with it participation. These data can be used to evaluate the thermodynamic properties of flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD).

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2. Experimental

2.1. Sample

Riboflavin was purchased from Fluka. For phase identification, an X-ray diffraction pattern of the vitamin B_2 sample was recorded on a Shimadzu X-ray diffractometer XRD-6000 (CuK_α radiation, geometry θ–2θ) in the 2θ range from 5° to 60° with scan increment of 0.02° (Fig. 1). The X-ray data and estimated impurity content (0.1 wt%) in the substance led us to conclude that the riboflavin sample studied was an individual crystalline compound (modification I [4]).

2.2. Apparatus and measurement procedure

To measure the heat capacity C_p^o of the tested substance in the range from 6 to 330 K a BKT-3.0 automatic precision adiabatic vacuum calorimeter with discrete heating was used. The calorimeter design and the operation procedure were described earlier [5]. The calorimeter was tested by measuring the heat capacity of high-purity copper and reference samples of synthetic

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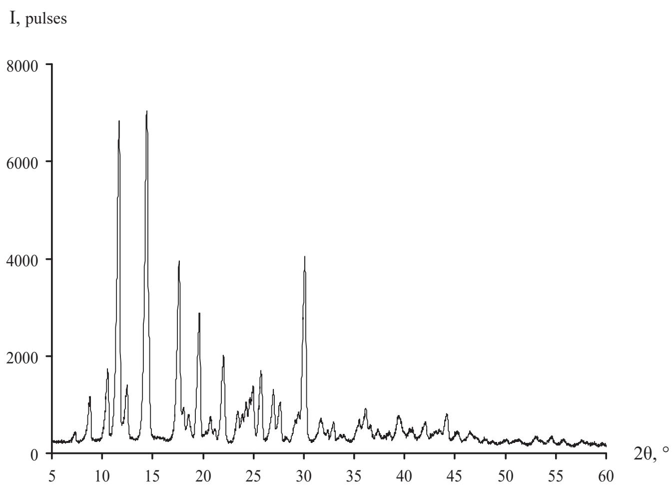

Fig. 1. X-ray diffraction patterns for riboflavin (modification I).

corundum and K-2 benzoic acid. The analysis of the results showed that measurement error of the heat capacity of the substance at helium temperatures was within ±2%, then it decreased to ±0.5% as the temperature was rising to 40 K, and was equal to ±0.2% at $T > 40$ K.

The energy of combustion, $\Delta_c U$, of riboflavin was measured in a calorimeter (V-08) with a static bomb and an isothermal shield. The calorimeter design, the procedure of measuring the energies of combustion and the results of calibration and testing are given elsewhere [6]. It should be noted that while checking the calorimeter by burning succinic acid, prepared at D.I. Mendeleev Research Institute of Metrology (the value of the standard enthalpy of combustion of the acid coincided with the certificate value within ±0.017%). For complete combustion of riboflavin we used paraffin as an auxiliary substance.

3. Results and discussion

3.1. Heat capacity

The C_p^o measurements were carried out between 6 and 322 K (Table 1). The mass of the sample loaded in the calorimetric ampoules of the BKT-3.0 device was 0.3779 g. 122 experimental C_p^o values were obtained in two series of experiments. The heat capacity of the sample varied from 20% to 50% of the total heat capacity of calorimetric ampoule + substance over the range between 6 and 322 K. The experimental points of C_p^o in the temperature interval 20–322 K were fitted by means of the least-squares method and polynomial equations (Eqs. (1)–(2)) of the C_p^o versus temperature have been obtained. The corresponding coefficients (A, B, C, etc.) are given in Table 2.

$$C_p^o = A + B\cdot\left(\frac{T}{30}\right) + C\cdot\left(\frac{T}{30}\right)^2 + D\cdot\left(\frac{T}{30}\right)^3 + E\cdot\left(\frac{T}{30}\right)^4 + F\cdot\left(\frac{T}{30}\right)^5 + G\cdot\left(\frac{T}{30}\right)^6 + H\cdot\left(\frac{T}{30}\right)^7 \quad (1)$$

$$C_p^o = A + B\cdot\ln(T/30) + C\cdot\ln^2(T/30) + D\cdot\ln^3(T/30) + E\cdot\ln^4(T/30) + F\cdot\ln^5(T/30) + G\cdot\ln^6(T/30) + +H\cdot\ln^7(T/30) + I\cdot\ln^8(T/30) + J\cdot\ln^9(T/30) + K\cdot\ln^{10}(T/30) + L\cdot\ln^{11}(T/30) + M\cdot\ln^{12}(T/30) + +N\cdot\ln^{13}(T/30) + O\cdot\ln^{14}(T/30) + P\times\ln^{15}(T/30) + Q\cdot\ln^{16}(T/30) \quad (2)$$

Table 1
Experimental values of isobaric heat capacities (J K^{-1} mol^{-1}) of crystalline riboflavin; M = 376.3682 g mol^{-1}.

T (K)	C_p^o	T (K)	C_p^o	T (K)	C_p^o
Series 1		50.55	79.52	119.63	194.3
6.75	2.55	52.99	83.98	122.64	198.5
7.32	2.83	55.45	88.71	125.66	202.7
8.41	3.45	57.93	93.42	128.69	207.3
8.94	4.08	60.48	98.18	131.70	211.6
9.34	4.48	62.91	102.6	134.72	215.9
9.68	4.81	65.40	106.9	137.75	220.3
10.15	5.25	67.89	110.9	140.77	224.6
10.36	5.42	70.37	115.1	143.80	229.0
10.98	6.23	72.85	119.2	146.83	233.0
11.56	7.05	75.32	123.3	149.86	237.2
11.98	7.68	77.79	128.2	152.90	241.7
13.16	9.25	80.34	132.4	155.94	246.0
15.03	12.22	82.75	137.1	158.98	250.1
16.92	15.24	85.22	141.4	162.02	254.2
18.77	18.25	88.86	147.9	165.06	258.6
20.65	21.38	Series 2		168.10	263.0
22.79	25.35	83.48	138.3	171.14	267.3
24.95	29.29	86.72	144.2	174.19	271.6
27.13	33.81	89.48	148.9	177.26	276.0
29.37	38.36	92.71	153.8	180.30	279.9
31.61	42.49	95.70	158.4	183.34	283.9
33.91	47.31	98.70	162.9	186.38	288.1
36.25	51.78	101.67	167.8	189.42	291.9
38.52	56.45	104.65	172.4	192.46	296.2
40.96	60.98	107.64	177.1	195.50	300.5
43.38	65.91	110.63	181.6	198.54	305.0
45.72	70.28	113.62	185.8	201.58	308.7
48.12	74.84	116.63	190.1	204.61	313.0
207.64	317.5	247.25	371.5	286.78	425.5
210.68	321.4	250.29	375.6	289.80	429.8
213.72	325.8	253.34	379.8	292.82	434.0
216.77	330.0	256.38	383.9	295.84	438.2
219.81	334.0	259.42	388.4	298.86	442.2
222.86	338.3	262.46	392.5	302.37	447.3
225.93	342.3	265.50	396.6	306.36	453.1
228.98	346.6	268.54	400.6	310.36	459.1
232.02	350.4	271.58	404.8	314.34	464.5
235.06	355.0	274.65	409.2	318.32	470.0
238.11	359.4	277.69	413.5	322.29	474.7
241.15	363.5	280.72	417.4		
244.20	367.7	283.75	421.5		

Their root mean square deviation from the averaging $C_p^o = f(T)$ curve was ±0.15% in the range T = (6–40) K, ±0.075% from T = (40 to 80) K and ±0.050% between T = (80 and 322) K. The experimental values of the molar heat capacity of riboflavin over the range from 6 to 322 K and the averaging $C_p^o = f(T)$ plot are presented in Fig. 2. The heat capacity C_p^o of this substance gradually increases with rising temperature and does not show any peculiarities.

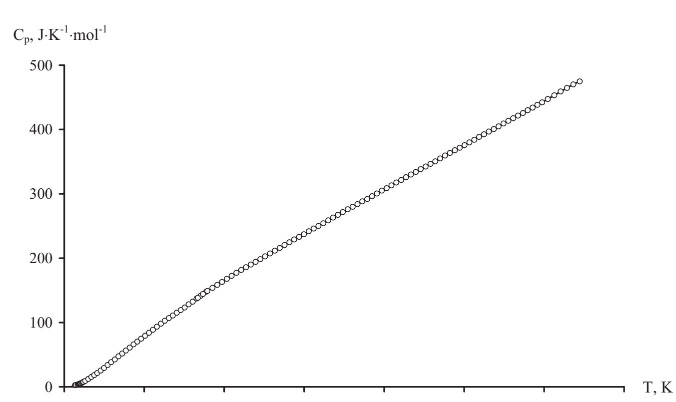

Fig. 2. Temperature dependence of heat capacity of riboflavin.