

■ Study of the properties of vitamins

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INTRODUCTION

Riboflavin, cyanocobalamin and nicotinic acid are water-soluble B vitamins that play important roles in cell metabolism. They have a key role in the normal functioning of the brain and nervous system. B vitamins are widely used in medicine, in food industry, in production of cosmetics. The goals of this work include calorimetric determination of the standard thermodynamic functions of the B vitamins with the purpose of describing biochemical and industrial processes with its participation.

MATERIALS AND METHODS

Riboflavin, cyanocobalamin and nicotinic acid were purchased from Fluka. According to the certificate of Fluka the content of impurities (0.1 wt %) led us to conclude that the samples studied were an individual crystalline compounds.

For phase identification, an X-ray diffraction patterns of the vitamin samples were 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°.

To measure the heat capacity of the tested substances in the range from 5 to 340 K a BKT-3.0 automatic precision adiabatic vacuum calorimeter with discrete heating was used. The calorimeter was tested by measuring the heat capacity of high-purity copper and reference samples of synthetic 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 $\pm 2\%$, then it decreased to $\pm 0.5\%$ as the temperature was rising to 40 K, and was equal to $\pm 0.2\%$ at $T > 40$ K. The energy of combustion, ΔcU , of compounds were measured in a calorimeter (V-08) with a static bomb and an isothermal shield. 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 $\pm 0.017\%$).

Thermal analysis was carried out with a Setaram LABSYS DSC 1600 differential scanning calorimeter in an argon atmosphere at a heating rate of 0.0833 K•s⁻¹.

The low-temperature X-ray diffraction was carried out on a Shimadzu X-ray diffractometer XRD-6000 (Cu K α radiation, geometry θ - 2θ) in the 2θ range from 5° to 60° with scan increment of 0.02° using Attachment TTK-450 (Anton Paar) in the temperature interval from 150K to 450K.

RESULTS AND DISCUSSION

The temperature dependences of heat capacity of riboflavin (C₁₇H₂₀N₄O₆), cyanocobalamin (C₆₃H₈₉CoN₁₄O₁₄P) and nicotinic acid (C₅H₄N-COOH) have been measured in the range from 7 to 330 K, from 6 to 343 K and from 5 to 346 K, respectively [1-3]. The heat capacity for all substances gradually increases with rising temperature and does not show any peculiarities (see Figure 1).

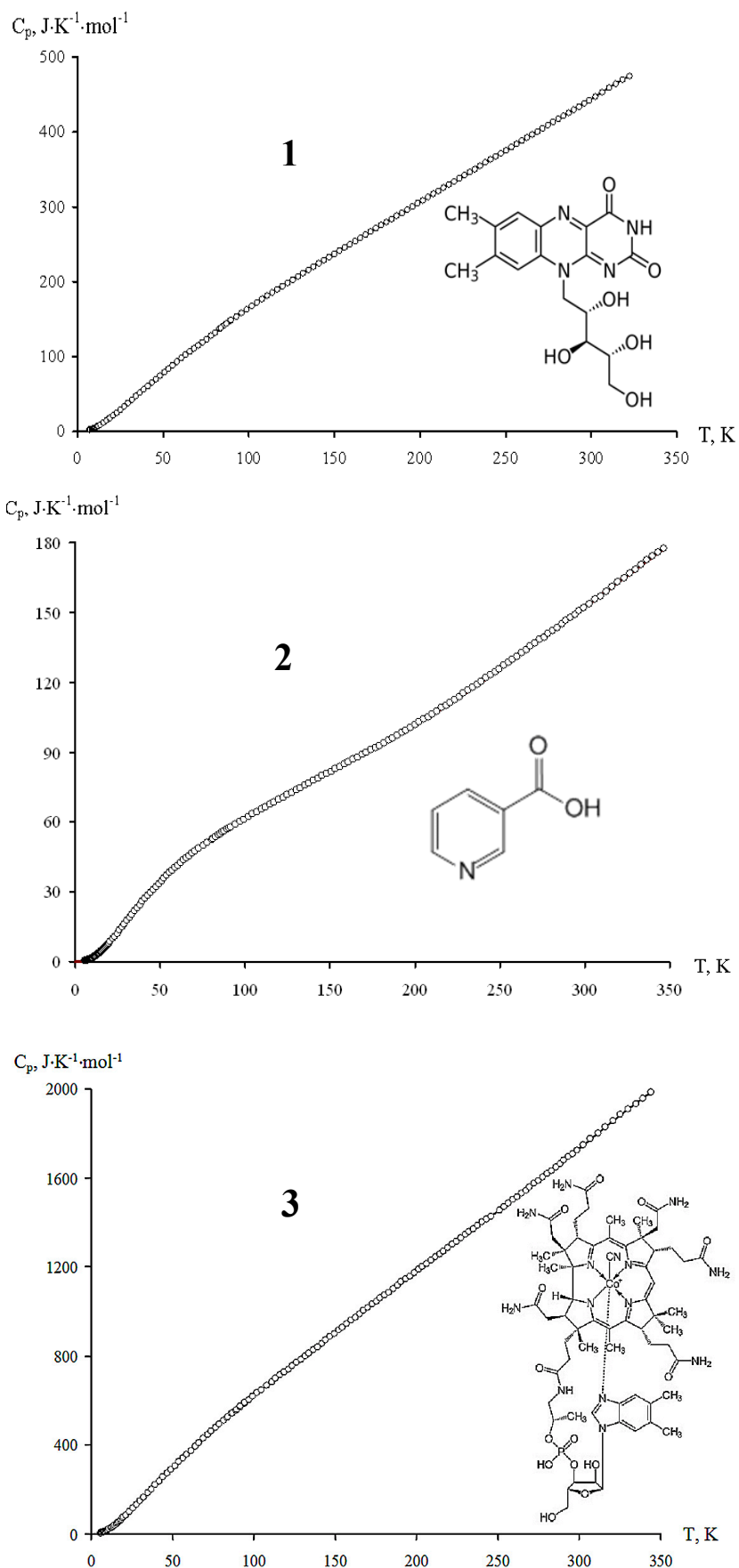


Figure 1. Temperature dependences of heat capacity of vitamins (1 – riboflavin, 2 – nicotinic acid, 3 – cyanocobalamin).

Table 1. Fractal dimensions and characteristic temperatures of vitamins

Compound	D	θ_{\max}
C ₁₇ H ₂₀ N ₄ O ₆	2.0	182.6
C ₅ H ₄ N-COOH	2.2	192.7
C ₆₃ H ₈₉ CoN ₁₄ O ₁₄ P	1.8	223.0

From the experimental heat capacity values in the range 20–40K the value of the fractal dimension D of the riboflavin was evaluated. According to the fractal theory of the heat capacity [4], D is the most important parameter that specifies the character of heterodynamics of the substance structure. For solids of a chain structure the relation heat capacity versus T at lower temperatures is proportional to T¹, of a layer structure to T² and of steric one to T³. In the fractal theory of the heat capacity, an exponent on T is the heat capacity function is denoted by D and is called the fractal dimension. This follows specifically from Eq. (1) [4]:

$$C_v = 3D(D+1)kNg^{(D+1)}x^{(D+1)}(T/q_{\max})^D \quad (1)$$

Where N is the number of atoms in a formula unit, k the Boltzmann constant, $g^{(D+1)}$ the g - function, $x^{(D+1)}$ the Riemann x-function, and q_{\max} is the characteristic temperature. As follows from inferences [4], D can be evaluated from the experimental data on the temperature-dependent heat capacities from a slope of the corresponding rectilinear sections of the plot $\ln C_v$ versus $\ln T$. From the $\ln C_v$ versus $\ln T$ plot and Eq. (1) it was found that in the range 20–40 K, D and θ_{\max} for vitamins. With these values of D and θ_{\max} Eq. (1) reproduces the experimental heat capacity values in the temperature range mentioned with an uncertainty of $\pm 0.93\%$. The D-value points to the layer structure of vitamins (table 1).

To calculate the standard thermodynamic functions of vitamins, heat capacity values of it were extrapolated from the starting temperature of the measurement (approximately 7 K) to 0 K by Debye's function of heat capacity [5]:

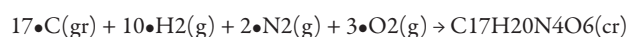
$$= nD(q_D/T), \quad (2)$$

where D is the symbol of Debye's function, n and q_D are specially selected parameters [5]. Eq. (2) with the above parameters describes the experimental heat capacity values of the compound between 7 and 10 K.

The energies and enthalpies of combustion of riboflavin at $T = 298.15\text{K}$ and standard pressure were determined. The values are for the reaction: $\text{C}_{17}\text{H}_{20}\text{N}_4\text{O}_6(\text{cr}) + 19\bullet\text{O}_2(\text{g}) \rightarrow 17\bullet\text{CO}_2(\text{g}) + 10\bullet\text{H}_2\text{O}(\text{l}) + 2\bullet\text{N}_2(\text{g})$

In brackets are given the physical states of reagents: (cr), crystalline; (g), gaseous; (l), liquid.

The data on the enthalpy of combustion of the crystalline riboflavin was used to estimate enthalpy of combustion and formation at $T = 298.15\text{K}$ and $p = 0.1\text{MPa}$. From the absolute value of the entropy of the riboflavin, carbon in the form of graphite, gaseous hydrogen, oxygen and nitrogen the standard entropy of formation $\Delta_f S^\circ$ of riboflavin at $T = 298.15\text{K}$ was calculated by. The Gibbs function of formation $\Delta_f G^\circ$ of the riboflavin was evaluated from the $\Delta_f H^\circ$ and $\Delta_f S^\circ$ values (Table 5). The values conform to the following process:



Where in the brackets are indicated the physical states of reagents: (gr), graphite; (g), gaseous; (cr), crystalline.

The enthalpies of combustion $\Delta_c H^\circ$ and the thermodynamic parameters of formation $\Delta_f H^\circ$, $\Delta_f S^\circ$, $\Delta_f G^\circ$ of the vitamins from the simple substances at $T = 298.15\text{K}$ and $p = 0.1\text{MPa}$ have been calculated (table 2).

Table 2. Enthalpies of combustions and thermodynamic characteristics of formation of vitamins

Compound	$-\Delta_c H^\circ$ (kJ·mol ⁻¹)	$-\Delta_f H^\circ(298)$ (kJ·mol ⁻¹)	$-\Delta_f S^\circ(298)$ (J·K ⁻¹ ·mol ⁻¹)	$-\Delta_f G^\circ(298)$ (kJ·mol ⁻¹)
C ₁₇ H ₂₀ N ₄ O ₆	8116 ± 13	1432 ± 13	1961 ± 3	847 ± 14
C ₅ H ₄ N-COOH	-	344.9 ± 0.9	503 ± 3	195 ± 2
C ₆₃ H ₈₉ CoN ₁₄ O ₁₄ P	-	-	7281 ± 5	-

Thermal analysis made it possible to establish some peculiarities of processes taking place in the compound under investigation during heating. Figure 2 represents DSC curve of cyanocobalamin, where we can see three endothermic effects at 504, 522, 530 K. These effects are connected with the decomposition of ligands coordinated to the cobalt atom. Already after the first effect, we observed a change in the color of dark red crystals of cyanocobalamin on black amorphous powder, which we confirmed X-ray diffraction data.

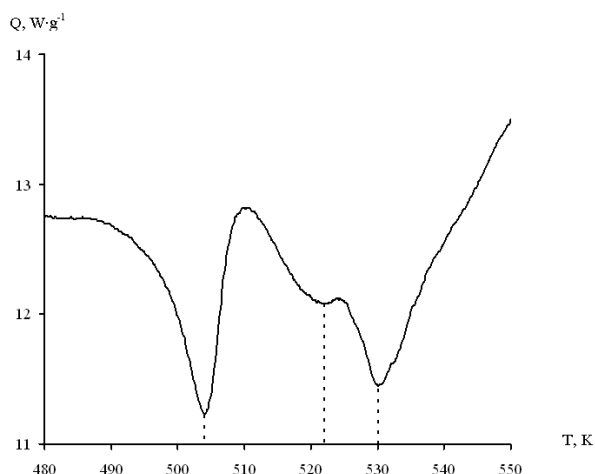


Figure 2. DSC curve of cyanocobalamin.

Next task of the work was the X-ray diffraction investigation of nicotinic acid with the purpose of definition of the thermal expansion coefficients. The temperature dependence of the unit cell parameters is described by the following polynomial:

$$\begin{aligned}
 a &= 3.956 \cdot 10^{-8} \cdot T^2 - 3.88482 \cdot 10^{-4} \cdot T + 7.30487 \quad (150 \leq T \leq 425 \text{ K}) \\
 b &= 6.2817 \cdot 10^{-7} \cdot T^2 + 4.05794 \cdot 10^{-4} \cdot T + 11.60223 \quad (150 \leq T \leq 425 \text{ K}) \\
 c &= 1.55045 \cdot 10^{-6} \cdot T^2 - 8.1159 \cdot 10^{-5} \cdot T + 7.15296 \quad (150 \leq T \leq 425 \text{ K}) \\
 \beta &= 6.1099 \cdot 10^{-6} \cdot T^2 - 1.20461 \cdot 10^{-2} \cdot T + 116.3819 \quad (150 \leq T \leq 425 \text{ K}) \\
 V &= 1.3462 \cdot 10^{-4} \cdot T^2 + 3.2271 \cdot 10^{-2} \cdot T + 543.831 \quad (150 \leq T \leq 425 \text{ K}).
 \end{aligned}$$

The unit cell parameters with increasing temperature change according to the most characteristic behavior of monoclinic unit cells. For example, we observe a decrease in the monoclinic angle and tend to form a right angle with increasing temperature. This behavior is characteristic of the monoclinic unit cells.

Thermal expansion coefficient is the quantitative characteristic of thermal expansion. We used the formula $\alpha L = 1/L \cdot (\Delta L / \Delta T)$, where αL - coefficient of thermal expansion, L - unit cell parameter. Value of the thermal expansion coefficient in given direction corresponds to length of radius-vector, which is traced from origin of coordinates to edge of figure of expansion. The thermal expansion of the nicotinic acid is anisotropic, and its thermal expansion coefficient depends significantly on temperature. We found that the anisotropy of thermal expansion increases with increasing temperature, and along the crystallographic axis a occurs even compression of the structure. For the construction of 3D version of the thermal expansion diagram algorithm for MapleSoft® can be used [6] (Figure 3). These figures allow presenting the anisotropy of the thermal expansion of the crystal at a certain temperature. We observe a considerable increase in the thermal expansion figures, which indicates low-energy hydrogen bonds between the molecules in the crystal nicotinic acid.

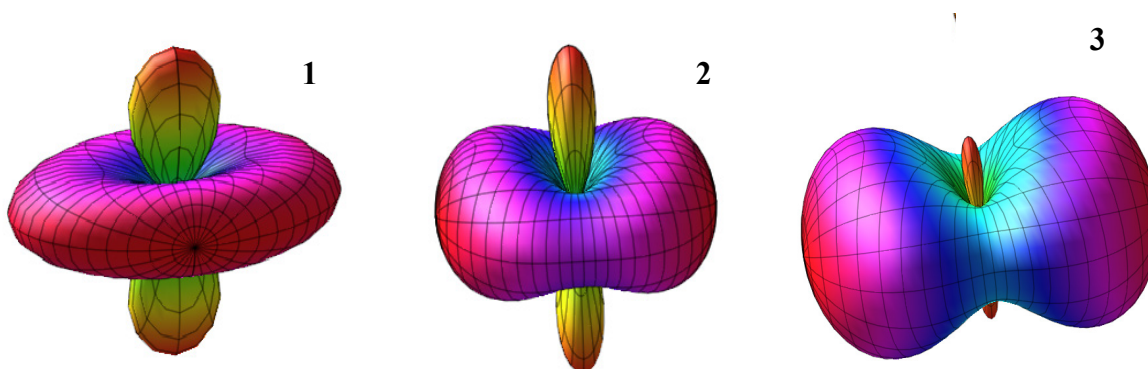


Figure 3. 3D thermal expansion diagrams for nicotinic acid (1 - at T=150K, 2 - at T=200K, 3 - at T=425 K).

CONCLUSIONS

The general aim of these investigations was to report the results of the thermodynamic study of vitamins. The heat capacity of vitamins is measured in the temperature range from 5 to 350K, the thermodynamic functions are calculated and the fractal dimensions D are evaluated. Thermochemical parameters of formation are determined by using combustion calorimetry. The thermodynamic analysis of reactions and low-temperature X-ray diffraction was made.

ACKNOWLEDGEMENTS

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