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Combustion Calorimetry and Thermodynamic Functions of Cyanocobalamin

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I. Introduction

Cyanocobalamin, also called vitamin B_{12} (PubChem CID: 5479203), is a water-soluble vitamin with a key role in the normal functioning of the brain and nervous system, and for the formation of blood. Vitamin B_{12} is a cobalt-containing compound synthesized by bacteria and an essential nutrient in mammals, which take it up from diet [1]. The significance of vitamin B_{12} adequate nutritional status throughout life span is established and the adverse effects of vitamin B_{12} deficiency in human health are currently recognized [2-4]. In addition to the well-described reversible hematological and often irreversible neurological changes of severe vitamin B_{12} deficiency, epidemiological studies revealed a more common condition, the low vitamin B_{12} status particularly in elder and pregnant women [5-6]. Because vitamin B_{12} is essential for DNA synthesis and cellular energy production, a low vitamin B_{12} status may be a risk factor for altered cellular metabolism and age-related diseases including cognitive decline and cardio-vascular disease [7].

This work is a continuation of systematic studies of vitamins B. Earlier in the articles [8-10], we have investigated the thermodynamic properties of vitamins B_2, B_3 and the temperature dependence of the heat capacity of cyanocobalamin. The goals of this work include calorimetric determination of the standard thermodynamic functions of the cyanocobalamin.

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II. Experimental

i. *Sample*

Cyanocobalamin was purchased from Fluka. For phase identification, an X-ray diffraction pattern of the vitamin B_{12} 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°. The X-ray data and estimated impurity content (0.1 wt %) in the substance led us to conclude that the cyanocobalamin sample studied was an individual crystalline compound. Cyanocobalamin can crystallize in three modifications [4]: 1) "as-purchased"; 2). "wet"; 3) "dry". According to X-ray diffraction and solid-state NMR spectroscopy, we investigated the "as-purchased" sample cyanocobalamin. This sample is usually obtained by rapid crystallization from water at 343 K.

ii. *Apparatus and measurement procedure*

The energy of combustion, $\Delta_c U$, of cyanocobalamin 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 [11]. 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 cyanocobalamin we used paraffin as an auxiliary substance.

Physico-chemical methods established the products of combustion of cyanocobalamin in the conditions of calorimetric experiment. Firstly, the solid products of combustion were identified by X-ray diffraction (Shimadzu X-ray diffractometer XRD-6000). Secondly, the formed liquid droplets were analyzed for phosphorus content using atomic absorption spectrophotometry (Shimadzu atomic absorption spectrophotometer AA-6300). Thirdly, the liquid droplets were titrated for total inorganic acids (Mettler Toledo pH meter Five Easy FE-20). Fourthly, the analysis of the gas phase was carried out by gas chromatography (Shimadzu GC 2010 Plus).

III. Results and Discussion

The experimental data on burning of cyanocobalamin are presented in Table 1. As a result, the energies and enthalpies of combustion of riboflavin at T = 298.15K and standard pressure were determined. The values are for the reaction:

$$C_{63}H_{88}CoN_{14}O_{14}P(cr)+79.75\cdot O_2(g)\rightarrow 63\cdot CO_2(g)+42.875\cdot H_2O(l)+0.75\cdot CoO(cr)+$$
$$+0.125\cdot Co_2P_2O_7(cr)+0.75\cdot H_3PO_4(sl\text{-}n,700H_2O)+7\cdot N_2(g)$$

In brackets are given the physical states of reagents: (cr), crystalline; (g), gaseous; (l), liquid; (sl-n), solution. It should be noted that we have used a significant amount of physico-chemical methods (see section 2.2) in the study of combustion products of cyanocobalamin which is an organometallic compound. The data on the enthalpy of combustion of the crystalline cyanocobalamin was used to estimate enthalpy of combustion and formation at T = 298.15K and p = 0.1MPa (Table 2). Due to the fact that the standard enthalpy of formation of dicobalt diphosphate absent in the literature, we calculated the standard enthalpy and entropy of formation of $Co_2P_2O_7$ at 298.15 K (Table 2). In works [12, 13], the absolute entropy and the standard Gibbs function of formation of dicobalt diphosphate were determined.

The Gibbs function of formation $\Delta_fG°$ of the cyanocobalamin was evaluated from the $\Delta_fH°$ and $\Delta_fS°$ [10] values (Table 2). The values conform to the following process:

$$63\cdot C(gr)+44\cdot H_2(g)+7\cdot N_2(g)+7\cdot O_2(g)+Co(cr)+P(cr)\rightarrow C_{63}H_{88}CoN_{14}O_{14}P(cr)$$

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

IV. Conclusions

The general aim of these investigations was to report the results of the thermodynamic study of the cyanocobalamin. The standard enthalpy of formation is determined by using combustion calorimetry. Much of the work is devoted to the study of the mechanism of combustion of cyanocobalamin and determination of thermodynamic functions of the combustion products.

V. Acknowledgements

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Table 1 : Experimental data on combustion energy for cyanocobalamin at $T = 298.15$K

Value	Experiment					
	1	2	3	4	5	6
m_{sam} (g) [a]	0.15345	0.1600	0.1466	0.1580	0.1595	0.1607
m_{par} (g) [a]	0.6920	0.6989	0.7024	0.7021	0.7050	0.7059
m_{thread} (g) [a]	0.0025	0.0022	0.00235	0.00215	0.0021	0.0019
W ($J \cdot K^{-1}$) [b]	14805	14805	14805	14805	14805	14805
Δt (K) [c]	2.443105	2.475455	2.463935	2.483210	2.493200	2.497915
$-\Delta_c U_{\Sigma}$ (J) [d]	36170.4	36649.1	36478.6	36763.9	36911.8	36981.6
$-\Delta_c U_{par}$ (J) [e]	32347.1	32668.2	32831.8	32818.7	32954.3	32997.3
$-\Delta_c U_{thread}$ (J) [e]	42.0	36.5	39.3	36.0	35.6	32.1
$-\Delta_c U_{HNO3}$ (J) [f]	5.9	10.5	8.2	8.8	9.4	11.7
$-\Delta_c U_C$ (J) [g]	9.8	16.4	16.4	-	26.2	26.2
$-\Delta_c U$ ($J \cdot g^{-1}$) [h]	24666.0	24689.4	24663.7	24686.1	24694.0	24683.9

$-\Delta_c \overline{U} = 24681 \pm 10$ $J \cdot g^{-1} = 33452 \pm 14$ $kJ \cdot mol^{-1}$, the mean energy of combustion of cyanocobalamin, $-\Delta_c U^\circ = 33435 \pm 14$ $kJ \cdot mol^{-1}$, the energy of combustion of cyanocobalamin at standard pressure.

[a] m_{sam}, m_{par}, m_{thread}, masses of the tested sample, paraffin and a cotton thread, respectively.

[b] W, the energy equivalent of the calorimeter.

[c] Δt, the temperature increase in the experience, adjusted for heat transfer.

[d] $\Delta_c U_{\Sigma}$, the total energy released during the experiment.

[e] $\Delta_c U_{par}$, $\Delta_c U_{thread}$, amounts of energy released on burning paraffin and cotton thread, respectively.

[f] $\Delta_c U_{HNO3}$, the energy of formation of nitric acid.

[g] $\Delta_c U_C$, the energy incomplete combustion of carbon.

[h] $\Delta_c U$, the energy released on burning of cyanocobalamin.

Table 2 : Enthalpy of combustion and thermodynamic characteristics of formation of cyanocobalamin and dicobalt diphosphate ($T = 298.15$ K. $p = 0.1$MPa)

Compound	$-\Delta_c H^\circ$ ($kJ \cdot mol^{-1}$)	$-\Delta_f H^\circ$ ($kJ \cdot mol^{-1}$)	$-\Delta_f S^\circ$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$-\Delta_f G^\circ$ ($kJ \cdot mol^{-1}$)
$C_{63}H_{88}CoN_{14}O_{14}P$	33459 ± 14	5017 ± 15	7281 ± 5 [10]	2846 ± 15
$Co_2P_2O_7$	–	2273 ± 7	654.3 ± 1.2	2078 ± 7 [13]

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