Combustion Calorimetry and Thermodynamic Functions of Cyanocobalamin

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Abstract- In a calorimeter with a static bomb and an isothermal shield, the energy of combustion of the cyanocobalamin has been measured at 298.15 K. Physico-chemical methods established the products of combustion of cyanocobalamin in the conditions of calorimetric experiment. The enthalpy of combustion $\Delta_{c}H^\circ$ and the thermodynamic parameters $\Delta_{f}H^\circ$, $\Delta_{f}G^\circ$ of the cyanocobalamin at $T = 298.15\, K$ and $p = 0.1\, MPa$ have been calculated. Thermodynamic parameters $\Delta_{f}H^\circ$, $\Delta_{f}S^\circ$ were determined and used to calculate the enthalpy of formation of cyanocobalamin.

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Strictly as per the compliance and regulations of:
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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.

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$_{\alpha}$ radiation, geometry 0-2θ in the 2θ range from 5º to 60º with scan increment of 0.02º). 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, $\Delta U$, 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 $\pm 0.017\%$). 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

\[
C_{63}H_{88}CoN_{14}O_{14}P(cr) + 79.75\text{O}_2(g) \rightarrow 63\text{CO}_2(g) + 42.875\text{H}_2\text{O}(l) + 0.75\text{CoO}(cr) + 0.125\text{Co}_2\text{P}_2\text{O}_7(cr) + 0.75\text{H}_3\text{PO}_4(sl-n,700\text{H}_2\text{O}) + 7\text{N}_2(g)
\]

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 \(T = 298.15\text{K}\) and \(P = 0.1\text{MPa}\) (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 \(\text{Co}_2\text{P}_2\text{O}_7\) 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 \(\Delta G^\circ\) of the cyanocobalamin was evaluated from the \(\Delta H^\circ\) and \(\Delta S^\circ\) \([10]\) values (Table 2). The values conform to the following process:

\[
63\text{C}(gr) + 44\text{H}_2(g) + 7\text{N}_2(g) + 7\text{O}_2(g) + \text{Co}(cr) + \text{P}(cr) \rightarrow C_{63}H_{88}CoN_{14}O_{14}P(cr)
\]

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 enthalphy 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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References Références Referencias

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

<table>
<thead>
<tr>
<th>Value</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{sam}$ (g)</td>
<td>0.15345</td>
<td>0.1600</td>
<td>0.1466</td>
<td>0.1580</td>
<td>0.1595</td>
<td>0.1607</td>
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<tr>
<td>$m_{par}$ (g)</td>
<td>0.6920</td>
<td>0.6989</td>
<td>0.7024</td>
<td>0.7021</td>
<td>0.7050</td>
<td>0.7059</td>
</tr>
<tr>
<td>$m_{thread}$ (g)</td>
<td>0.0025</td>
<td>0.0022</td>
<td>0.00235</td>
<td>0.00215</td>
<td>0.0021</td>
<td>0.0019</td>
</tr>
<tr>
<td>$W$ (J·K$^{-1}$)</td>
<td>14805</td>
<td>14805</td>
<td>14805</td>
<td>14805</td>
<td>14805</td>
<td>14805</td>
</tr>
<tr>
<td>$\Delta t$ (K)</td>
<td>2.443105</td>
<td>2.475455</td>
<td>2.463955</td>
<td>2.483210</td>
<td>2.493200</td>
<td>2.497915</td>
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<tr>
<td>$-\Delta U_f$ (J)</td>
<td>36170.4</td>
<td>36649.1</td>
<td>36478.6</td>
<td>36763.9</td>
<td>36911.8</td>
<td>36981.6</td>
</tr>
<tr>
<td>$-\Delta U_{par}$ (J)</td>
<td>32347.1</td>
<td>32668.2</td>
<td>32831.8</td>
<td>32818.7</td>
<td>32954.3</td>
<td>32997.3</td>
</tr>
<tr>
<td>$-\Delta U_{thread}$ (J)</td>
<td>42.0</td>
<td>36.5</td>
<td>39.3</td>
<td>36.0</td>
<td>35.6</td>
<td>32.1</td>
</tr>
<tr>
<td>$-\Delta U_{HNO_3}$ (J)</td>
<td>5.9</td>
<td>10.5</td>
<td>8.2</td>
<td>8.8</td>
<td>9.4</td>
<td>11.7</td>
</tr>
<tr>
<td>$-\Delta U_C$ (J)</td>
<td>9.8</td>
<td>16.4</td>
<td>16.4</td>
<td>-</td>
<td>26.2</td>
<td>26.2</td>
</tr>
<tr>
<td>$-\Delta U$ (J·g$^{-1}$)</td>
<td>24666.0</td>
<td>24689.4</td>
<td>24663.7</td>
<td>24686.1</td>
<td>24694.0</td>
<td>24683.9</td>
</tr>
</tbody>
</table>

$-\Delta U_f = 24681 \pm 10$ J·g$^{-1} = 33452 \pm 14$ kJ·mol$^{-1}$, the mean energy of combustion of cyanocobalamin, $-\Delta cU_f = 33435 \pm 14$ kJ·mol$^{-1}$, the energy of combustion of cyanocobalamin at standard pressure.

$\Delta t$, the temperature increase in the experiment, adjusted for heat transfer.

$-\Delta U_f$, the total energy released during the experiment.

$\Delta U_{par}$, $\Delta U_{thread}$, amounts of energy released on burning paraffin and cotton thread, respectively.

$\Delta U_{HNO_3}$, the energy of formation of nitric acid.

$\Delta U_C$, the energy incomplete combustion of carbon.

$\Delta U$, 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)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\Delta H^o$ (kJ·mol$^{-1}$)</th>
<th>$-\Delta H^o$ (kJ·mol$^{-1}$)</th>
<th>$-\Delta S^o$ (J·K$^{-1}$·mol$^{-1}$)</th>
<th>$-\Delta G^o$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{63}$H$</em>{88}$Co$<em>{14}$N$</em>{14}$O$_{14}$P</td>
<td>33459 ± 14</td>
<td>5017 ± 15</td>
<td>7281 ± 5 [10]</td>
<td>2846 ± 15</td>
</tr>
<tr>
<td>Co$_3$P$_2$O$_7$</td>
<td>–</td>
<td>2273 ± 7</td>
<td>654.3 ± 1.2</td>
<td>2078 ± 7 [13]</td>
</tr>
</tbody>
</table>