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Thermochemistry of the dissolution of tetra-4-sulfophthalocyanine nickel in aqueous solutions KOH at 298.15 K

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CITATION

Krutova O, Maizlish V, Bazanov M, et al. Thermochemistry of the dissolution of tetra-4-sulfophthalocyanine nickel in aqueous solutions KOH at 298.15 K. Mechanical Engineering Advances. 2024; 2(1): 326.
<https://doi.org/10.59400/mea.v2i1.326>

ARTICLE INFO

Received: 14 December 2023
Accepted: 1 February 2024
Available online: 4 March 2024

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Abstract: We have obtained a nickel tetra-4-sulfophthalocyanine complex, soluble in water. The standard enthalpies of formation of a compound can be considered as the sum of the additive group contributions of fragments of these molecules. We assessed this value using a method based on group systematics with a Benson-type classification of fragments, taking into account the influence of the primary environment of the atoms. In order to obtain the value of the contribution of $E_{\text{compl}}(\text{N})_4\text{-Ni}$, we used the bomb calorimetry method. The enthalpy of combustion of tetrakis (4-methoxyphenyl) porphine and its complex with nickel tetrakis (4-methoxyphenyl) porphine nickel were experimentally determined. Thermal effects of dissolution of crystalline nickel tetra-4-sulfophthalocyanine in aqueous solutions of various KOH concentrations (from 0.002 to 0.02 mol·L⁻¹) at 298.15 K were determined by the direct calorimetric method. The measurements were carried out in a calorimeter with an isothermal shell equipped with a reaction vessel with a volume of 60 cm³, electric calibration at $T = (293.15\text{--}308.15) \pm 0.01$ K and $P = 100.5 \pm 0.7$ kPa, and automatic temperature registration. The standard enthalpy of formation of dissociation products of the tetra-4-sulfophthalocyanine complex with nickel in an aqueous solution has been calculated.

Keywords: thermodynamics; solutions; calorimeter; enthalpy; constant; phthalocyanines

Currently, studies of phthalocyanines (Pc) and their derivatives are intensively developing [1–5]. One of the directions of PC modification is the introduction of various substituents into the benzene rings of compounds. Currently, sulfophthalocyanines are used as dyes [6], effective catalysts for various redox reactions, models in the study of some biological processes [7], medicine, etc. [8–10]. There is no data in the literature on the enthalpies of dissolution of tetra-4-sulfophthalocyanines with nickel in aqueous solutions of alkalis. Despite the fact that this class of compounds is being studied very widely at present, it is known that the introduction of sulfo groups into the Pc molecule gives the compounds the ability to dissolve in aqueous solutions of alkalis. However, sulfophthalocyanines have been studied to a much lesser extent. We chose nickel as the complexing ion. Nickel ion is one of the important microelements for living organisms (bacteria, plants, animals, and humans). About biological the role of nickel (II) in an enzymatic catalyst (urease) more than 30 are known years.

In this work, the complexes of tetra-4-sulfophthalocyanine with nickel were chosen as the object of research (**Figure 1**).

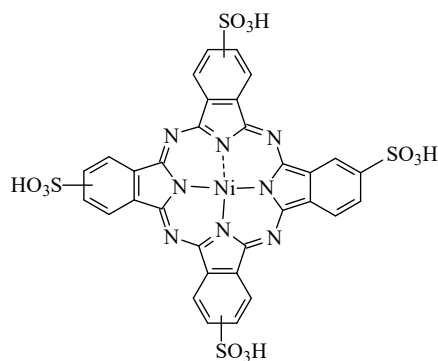


Figure 1. Tetra-4-sulfophthalocyanines nickel.

The aim of this work was to study standard enthalpies of the formation of complexes of tetra-4-sulfophthalocyanines with nickel and their dissociation products in aqueous solution by the thermal effects of dissolution of the preparations in water and in aqueous solutions of KOH at 298.15 K. We obtained data for calculating group contributions ($E_{\text{compl}}(\text{N})_4\text{-Ni}$) to the enthalpy of formation of tetra-4-sulfophthalocyanines with nickel using an additive scheme for the first time. The combustion enthalpies of Tetrakis(4-methoxyphenyl)porphine (1) and tetrakis(4-methoxyphenyl)nickel porphine (2) were determined experimentally using bomb calorimetry. From these data, the contribution of ($E_{\text{compl}}(\text{N})_4\text{-Ni}$) was isolated for the first time.

1. Experimental part

4-tetrasulfophthalocyanine with nickel was synthesized by the method of “urea fusion” [11]. The resulting melt was ground, dissolved in water, the solution was filtered, and the filtrate was evaporated. The substance was washed with concentrated hydrochloric acid to colorless filtrates and dried. The product was dissolved in water, the aqueous solution was passed through a column with KU-2-8 cationite, and then chromatographed using silica gel and molselect G-10 sequentially as an adsorbent, collecting the most colored zone. The resulting solution was evaporated, and the dry product was treated with organic solvents (methanol, acetone, and benzene) in a Soxhlet apparatus. Dried under vacuum at 373–383 K. Output: 37%. ESP, λ_{max} , nm (lgε) (DMSO): 665 (5.4), 610 (4.6), 336 (4.4), what corresponds to the literature data [11].

It is known that as a result of template synthesis, a mixture of randomizers is formed, the separation of which is a difficult task. In our case, the separation and isolation of individual randomers was not carried out.

The heat of dissolution of the investigated compound was determined experimentally in this work by the calorimetric method. The installation is described in detail in the work [12]. The operation of the installation was checked according to the calorimetric standard [13].

The heat of combustion was measured in a calorimeter of type B-08-MA with an isothermal shell, a stationary calorimetric bomb, and an improved measuring circuit, according to the method described earlier [14]. The temperature change in the calorimetric vessel was recorded using a platinum resistance thermometer included in the bridge circuit. The measured characteristic is the unbalance voltage of the bridge

(P-4053). The energy equivalent of the calorimeter, which was determined by burning K-1 benzoic acid, was 8348.5 ± 2.8 kJ/V. The initiation of the Gorenje reaction was carried out by discharging a capacitor onto a copper wire.

2. Results and discussion

It is advisable to use the Benson method to calculate the standard enthalpy of formation [15–17]. The calculation of the enthalpy of combustion and formation of the test compound was carried out according to the formula:

$$\Delta_{c(f)}H^0_{(cr)} = \sum_i^{\Pi} A_i \Delta_{c(f)}H_i^0, i = 1, 2, 3, \dots, n \quad (1)$$

where $\Delta_{c(f)}H^0_{(cr)}$ is the energy contribution to the enthalpy of combustion (formation) of a certain atomic group, A_i is the number of such atomic groups in the molecule, and n is the number of types of atomic groups in the molecule.

In the **Table 1**, the initial data for the calculation of $\Delta_f H^0_{cr}$ ($C_{32}H_{16}N_8O_{12}S_4Ni$) are presented.

Table 1. Numerical values of energy contributions to the values of the enthalpy of formation in accordance with the Benson classification.

№	Group	Number of groups (n)	$-\Delta_f H^0_{(cr.)}$, kJ·mol ⁻¹
1	(C) ₃ -CH	12	-19.9 ± 29.3
2	(C) ₃ -N	8	-102.0 ± 64.3
3	(C) ₄ -C	8	-9.4
4	(C) ₃ (S)-C	4	2.5
5	(N) ₃ (C)-C	8	-318.0
6	(C)-SO ₃ H	4	1495.4 ± 71.6
7	E _{compl} (N) ₄ -Ni	1	$840.25 \pm 14.32^*$

* experimentally determined in this paper.

In order to obtain the value of the contribution of E_{compl}(N)₄-Ni, we used the bomb calorimetry method. The enthalpy of combustion of tetrakis (4-methoxyphenyl) porphine and tetrakis (4-methoxyphenyl) nickel porphine was experimentally determined (**Figure 2**). The data are presented in **Tables 2** and **3**.

Table 2. Heat of combustion of tetrakis (4-methoxyphenyl) porphine.

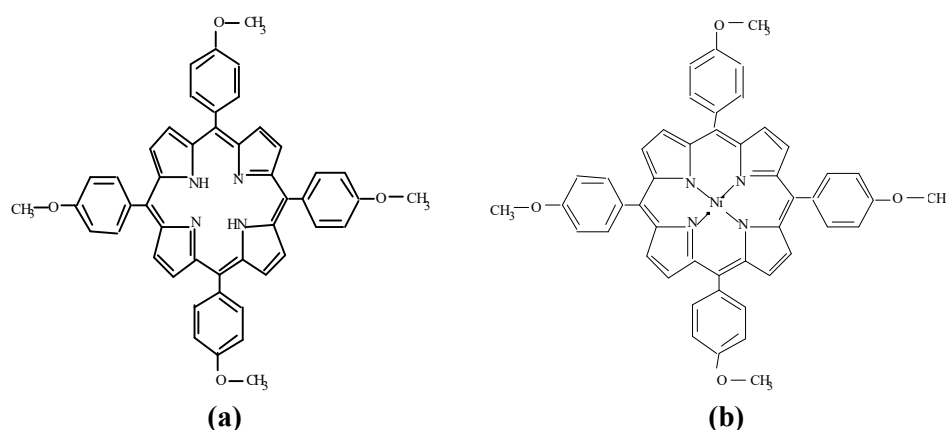
№	m_{TMPP} , g	ΔT_{ucp} , mkV	$\frac{m_{CO_2}^{exp.}}{m_{CO_2}^{calc.}}$	$q_{HNO_3} \cdot 10^{-3}$, kJ	$-\Delta_c U^B$, kJ·mol ⁻¹
1	0.0487	193.9609	1.0001	5.66	24,248
2	0.0515	204.5898	-	6.75	24,236
3	0.0783	310.6317	1.0002	7.16	24,258
4	0.0846	335.3150	0.9998	8.34	24,232
5	0.0944	374.3164	-	9.26	24,246

$-\Delta_c U^B_{cp} = 24,244 \pm 13$ kJ·mol⁻¹.

Table 3. Heat of combustion of tetrakis (4-methoxyphenyl) nickel porphine.

№	$m_{T(4-MeOPh)PnNi}$, g	$\Delta T_{\text{acup.}}$, mkV	$\frac{m_{CO_2}^{exp.}}{m_{CO_2}^{calc.}}$	$q_{HNO_3} \cdot 10^2$, kJ	$-\Delta_c U^B$, kJ·mol ⁻¹
1	0.03729	138.06	0.9989	3.12	24,233
2	0.05394	199.15	1.0003	4.05	24,229
3	0.05425	200.31	0.9998	4.06	24,231
4	0.05885	217.23	1.0001	4.42	24,238
5	0.06558	241.99	1.001	4.92	24,242

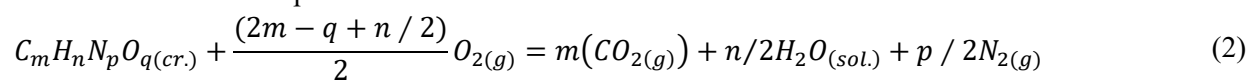
$$-\Delta_c U_{cp.}^B = 24,246 \pm 6 \text{ kJ} \cdot \text{mol}^{-1}.$$

**Figure 2.** (a) Tetrakis (4-methoxyphenyl) porphine; (b) tetrakis (4-methoxyphenyl) nickel porphine.

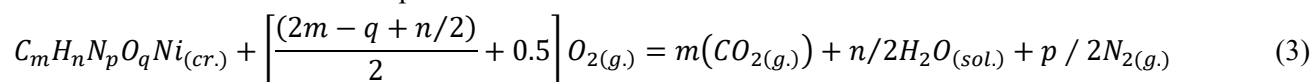
Compound (a) and (b) were obtained by Tarasov et al. [18].

Benzoic acid was used as an auxiliary substance for the difficult-to-burn compounds studied in this work. Therefore, when calculating the combustion energy, the correction for the heat of combustion of benzoic acid was taken into account.

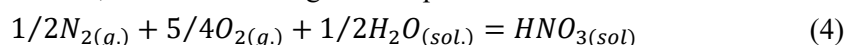
The values of the combustion energy of the studied compounds are attributed to combustion reactions, which can be represented by the following schemes: for organic compounds:



for complexes with metals:



Nitrogen, which is part of the compound, is released in free form (N₂) as a result of the combustion reaction, and only a small part of it is found in the final products in the form of nitric acid, formed according to the equation:



The thermal effect of reaction (3) at 298.15K and dilution of 1:500 H₂O is 64.0 kJ·mol⁻¹. When calculating the value of $\Delta_c U^B$, a corresponding correction was introduced for the heat of formation of a nitric acid solution.

The combustion energy of the studied compounds was determined by the formula:

$$-\Delta_c U_{(cr., 298 K)}^B = \frac{[W \cdot \Delta T_{cor.} - q_b - q_{HNO_3} - Q_{ac} \cdot m_{ac.}] \cdot M}{m} \quad (5)$$

where: W is the energy equivalent of a calorimeter, kJ/V; ΔT_{cor} —corrected temperature rise, V; q_b —correction for the heat of combustion of copper wire, kJ; q_{HNO_3} —correction for the heat of formation of a solution of nitric acid, kJ; Q_{ac} —the heat of combustion of benzoic acid, kJ/g; m_{ac} —weight of the benzoic acid sample, g; M —molar mass of the compound under study, g/mol; m —mass of the sample under study, g.

The errors in determining the values of the combustion heats of porphyrins and their structural analogues were calculated similarly to the errors of the energy equivalent of a calorimeter with a confidence probability of 0.95.

The value of $\Delta_c U^B$ obtained as a result of the experiment refers to the isothermal combustion reaction of the studied compounds under real conditions of the process. To calculate the change in the internal energy of the combustion reaction of a substance under standard conditions, that is, when all the starting substances and combustion products are at a pressure of 1×10^5 Pa and a temperature of 298 K, the Washburn correction was determined, which took into account the thermal effects of the compression processes of the gas and liquid phases of the bomb, the dissolution of CO_2 and O_2 in the liquid phase of the bomb, and the evaporation of water into the gas phase.

The standard enthalpy of combustion ($\Delta_c H^0$) of the studied compounds was calculated from the ratio:

$$\Delta_c H^0 = \Delta_c U^0 + \Delta n RT \quad (6)$$

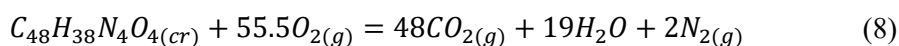
where: Δn is the change in the number of moles of gas in the chemical equation for the combustion process of substances.

The standard enthalpy of formation ($\Delta_f H^0$) of organic compounds was calculated by the formula:

For a complex with Ni, the calculation of $\Delta_f H^0$ was carried out according to the equation:

$$\begin{aligned} &\Delta_f H^0(C_m H_n N_p O_q M_{cr., 298K}) \\ &= m \Delta_f H^0(CO_{2,g, 298K}) + n/2 \Delta_f H^0(H_2O_{sol, 298K}) + \Delta_f H^0(MO_{cr., 298K}) \\ &- \Delta_c H^0(C_m H_n N_p O_q M_{k., 298K}) \end{aligned} \quad (7)$$

The value of $\Delta_c U^B_{(cr, 298 K)}$ refers to the combustion reaction of the TMPP under study:



According to experimental data, thermodynamic characteristics for tetrakis(4-methoxyphenyl) porphine are calculated using Equations (5), (7), and (8): $\Delta_c U^0 = -23,869 \pm 13$ kJ·mol⁻¹; $\Delta_c H^0 = -23,883 \pm 13$ kJ·mol⁻¹; $\Delta_f H^0 = -436.25 \pm 13$ kJ·mol⁻¹.

The value of $\Delta_c U^B_{(cr, 298 K)}$ is attributed to the combustion reaction T(n-MeOPh)Ni:

$$C_{48}H_{36}N_4O_4Ni_{(cr)} + 55.5O_{2(g)} = 48CO_2 + 18H_2O + NiO_{(cr)} + 2N_{2(g)} \quad (9)$$

During the combustion of the tablet of the drug under study, a precipitate of black NiO was formed; the amount of nickel and the composition of the precipitate were determined by atomic absorption analysis.

According to experimental data, the standard thermodynamic characteristics of the studied compound are calculated: $\Delta_c U^0 = -23,855 \pm 6$ kJ·mol⁻¹; $\Delta_c H^0 = -23,869 \pm 6$ kJ·mol⁻¹; $\Delta_f H^0 = -404 \pm 6$ kJ·mol⁻¹.

Based on the experimental values of the enthalpy of formation T(n-Me)Ph)P and its complex with Ni, the energy contribution associated with the complexation process is calculated. The calculation was carried out according to the formula:

$$E_{comp1.} = \Delta_f H^0_{(Me-EP-I)} - \Delta_f H^0_{(H_2EP-I)} \quad (10)$$

where: $\Delta_f H^0$ is the standard enthalpy of formation of the tetrakis (4-methoxyphenyl) porphine nickel complex $\text{kJ}\cdot\text{mol}^{-1}$;

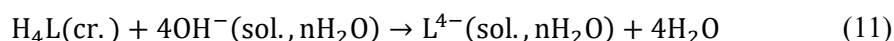
$\Delta_f H^0$ is the standard enthalpy of formation of tetrakis (4-methoxyphenyl) porphine, $\text{kJ}\cdot\text{mol}^{-1}$ (**Table 4**). Thus, $E_{compl.} = -840.25 \pm 14 \text{ kJ}\cdot\text{mol}^{-1}$.

Table 4. Values of standard enthalpies of formation and complex formation energies T(n-ME)PH)P and NiT(n-MeOPh)P.

Compound	$\Delta_f H^0, \text{kJ}\cdot\text{mol}^{-1}$	$E_{compl.}, \text{kJ}\cdot\text{mol}^{-1}$
T(n-MeOPh)P	436.25 ± 13	-
NiT(n-MeOPh)P	-404 ± 6	-840.25 ± 14.32

Based on the data obtained, we were able to calculate $\Delta_f H^0_{(cr.)(C_{32}H_{16}N_8O_{12}S_4Ni)} = -3158.1 \pm 101.6 \text{ kJ}\cdot\text{mol}^{-1}$.

The process of dissolving in a KOH solution can be represented by the following scheme:



The experimental data of thermal effects of the dissolution of crystalline tetra-4-sulfophthalocyanine in aqueous solutions KOH at 298.15 K are presented in **Figure 3**. Experimental data are given in **Table 5**.

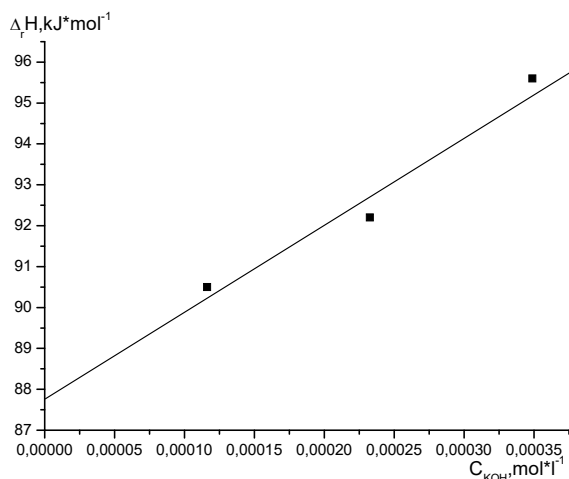


Figure 3. Graphical determination of the thermal effect of particle dissolution $H_4L(cr.)$ in KOH solution with infinite dilution.

Table 5. Enthalpy of solubility of nickel tetra-4-sulfophthalocyanine in KOH solution at various concentrations and $T = 298.15$ K.

$m \cdot 10^{-3}, \text{g}$	$C_{\text{кон.}} \text{ mol} \cdot \text{L}^{-1}$	$-\Delta_{\text{sol}}H \text{ kJ} \cdot \text{mol}^{-1}$
0.0010		90.53 ± 0.36
0.0013	1.165×10^{-4}	90.65 ± 0.38
0.0012		90.48 ± 0.38
0.0020		92.25 ± 0.35
0.0021	2.326×10^{-4}	92.32 ± 0.36
0.0020		92.19 ± 0.38
0.0030		95.68 ± 0.35
0.0032	3.489×10^{-4}	95.66 ± 0.37
0.0030		95.65 ± 0.35

Practical testing of the Debye-Hückel theory has been the subject of numerous experimental works, including precision measurements of activity coefficients, heats of dilution, etc. A sufficiently rigorous test of the theory can be made, naturally, only in the region of extremely dilute solutions, where one can expect compliance with the limit law [19]. To process our data, we used the Equation (12) proposed by Vasiliev [19]:

$$\Delta_r H_i - \Delta Z^2 \psi(I) = \Delta_r H_i^0 + bI, \quad (12)$$

where $\Delta_r H_i$ and $\Delta_r H_i^0$ are the thermal effects of process (11) at finite and zero values of the ionic strength.

Using the values of the standard enthalpies of formation of hydroxide ion $\Delta_f H^0$ (OH^- , sol., H_2O , std.s., 298.15 K) = $-230.04 \text{ kJ} \cdot \text{mol}^{-1}$ and water (H_2O) in an aqueous solution $\Delta_f H^0$ (H_2O , lig, 298.15 K) = $-285.83 \text{ kJ} \cdot \text{mol}^{-1}$, recommended by Glushko [20], we calculated the standard enthalpy of formation of the deprotonated L^{4-} ion:

$$\begin{aligned} \Delta_f H^0(\text{L}^{4-}, \text{sol.}, \text{H}_2\text{O}, \text{std. s.}, 298.15 \text{ K}) \\ = \Delta_f H^0(\text{H}_4\text{L}, \text{cr.}, 298.15\text{K}) + 4\Delta_f H^0(\text{OH}^-, \text{sol.}, \text{H}_2\text{O}, \text{std. s.}, 298.15\text{K}) + \Delta_f H^0_{(11)} \\ - 4\Delta_f H^0(\text{H}_2\text{O}, \text{liq.}, 298.15\text{K}) \end{aligned} \quad (13)$$

The standard enthalpies of formation of HL^{3-} , H_2L^{2-} , H_3L^- , H_4L particles in an aqueous solution were calculated using the equations:

$$\begin{aligned} \Delta_f H^0(\text{HL}^{3-}, \text{sol.}, \text{H}_2\text{O}, \text{std.}, \text{hyp.}, \text{nedis.}, 298.15\text{K}) \\ = \Delta_f H^0(\text{L}^{4-}, \text{sol.}, \text{H}_2\text{O}, \text{std.}, 298.15\text{K}) - \Delta_{\text{dis}} H^0(\text{HL}^{3-}, 298.15\text{K}) \end{aligned} \quad (14)$$

$$\begin{aligned} \Delta_f H^0(\text{H}_2\text{L}^{2-}, \text{sol.}, \text{H}_2\text{O}, \text{std.}, \text{hyp.}, \text{nedis.}, 298.15\text{K}) \\ = \Delta_f H^0(\text{HL}^{3-}, \text{sol.}, \text{H}_2\text{O}, \text{std.}, 298.15\text{K}) - \Delta_{\text{dis}} H^0(\text{H}_2\text{L}^{2-}, 298.15\text{K}) \end{aligned} \quad (15)$$

$$\begin{aligned} \Delta_f H^0(\text{H}_3\text{L}^-, \text{sol.}, \text{H}_2\text{O}, \text{std.}, \text{hyp.}, \text{nedis.}, 298.15\text{K}) \\ = \Delta_f H^0(\text{H}_2\text{L}^{2-}, \text{sol.}, \text{H}_2\text{O}, \text{std.}, 298.15\text{K}) - \Delta_{\text{dis}} H^0(\text{H}_3\text{L}^-, 298.15\text{K}) \end{aligned} \quad (16)$$

$$\begin{aligned} \Delta_f H^0(\text{H}_4\text{L}, \text{sol.}, \text{H}_2\text{O}, \text{std.}, \text{hyp.}, \text{nedis.}, 298.15\text{K}) \\ = \Delta_f H^0(\text{H}_3\text{L}^-, \text{sol.}, \text{H}_2\text{O}, \text{std.}, 298.15\text{K}) - \Delta_{\text{dis}} H^0(\text{H}_4\text{L}, 298.15\text{K}) \end{aligned} \quad (17)$$

The values of $\Delta_{\text{dis}} H^0(\text{H}_4\text{L}, 298.15 \text{ K})$, $\Delta_{\text{dis}} H^0(\text{H}_3\text{L}^-, 298.15 \text{ K})$, $\Delta_{\text{dis}} H^0(\text{H}_2\text{L}^{2-}, 298.15 \text{ K})$, $\Delta_{\text{dis}} H^0(\text{HL}^{3-}, 298.15 \text{ K})$, were calculated by using the HEAT [21,22] computer program. The obtained values are presented in **Table 6**.

Table 6. Enthalpy of stepwise dissociation of Pc at a temperature of 298.15 K ($\text{kJ}\cdot\text{mol}^{-1}$).

Process	$\Delta_r H_{\text{dis}}$, (complex Ni)	pK _i
$\text{H}_4\text{L} \rightarrow \text{H}_3\text{L}^- + \text{H}^+$	52.3 ± 1.5	1.93 ± 0.35
$\text{H}_3\text{L}^- \rightarrow \text{H}_2\text{L}^{2-} + \text{H}^+$	98.6 ± 1.7	4.89 ± 0.35
$\text{H}_2\text{L}^{2-} \rightarrow \text{HL}^{3-} + \text{H}^+$	114.8 ± 1.9	9.31 ± 0.35
$\text{HL}^{3-} \rightarrow \text{L}^{4-} + \text{H}^+$	162.3 ± 1.6	12.32 ± 0.35

The thermodynamic characteristics of the dissolution of porphyrins obtained in our works [23,24] will allow us to evaluate the influence of the metal ion of the complexing agent, as well as the influence of the isomerism of the position of functional groups in the benzene ring. The values of the standard enthalpy of formation of Pc in an aqueous solution were obtained in this work for the first time. Variations in the central ion and the structure of substituents in the Pc molecule make it possible to change its thermodynamic properties, which is confirmed, in particular, by data on the heats of dissolution of copper tetra-3-carboxyphthalocyanine in a KOH solution $\Delta_r H = -79.86 \pm 0.4 \text{ kJ/mol}$ and tetra-4-carboxyphthalocyanine copper $\Delta_r H = -78.33 \pm 0.4 \text{ kJ/mol}$ [23], the replacement of the central metal ion with zinc makes this difference even more noticeable $\Delta_r H(1) = -59.64 \pm 0.4 \text{ kJ/mol}$ [24]. The obtained values are presented in **Table 7**.

Table 7. Standard enthalpy of Pc formation and its dissociation products in Aqueous solution ($\text{kJ}\cdot\text{mol}^{-1}$).

Particles	Condition	$\Delta_r H^\circ(298.15 \text{ K})$, (complex Ni)
H_4L	cr.	-3158.1 ± 101.6
	sol., H_2O , st. s., hyp., nedis.	-3451.6 ± 101.6
H_3L^-	sol., H_2O , st. s., hyp., nedis.	-3398.3 ± 101.6
H_2L^{2-}	sol., H_2O , st. s., hyp., nedis.	-3299.7 ± 101.6
HL^{3-}	sol., H_2O , st. s., hyp., nedis.	-3184.9 ± 101.6
L^{4-}	sol, H_2O , st. s.	-3022.6 ± 101.6

Author contributions: Writing—original draft, writing—review and editing, OK; conceptualization, VM and MB; formal analysis, VC; project administration, AV; investigation, PK. All authors have read and agreed to the published version of the manuscript.

Funding: The work was carried out at the Research Institute of Thermodynamics and Kinetics of Chemical Processes of the Ivanovo State University of Chemical Technology within the framework of the State Assignment (basic part), project № FZZW-2023-0008. The study was carried out using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT (with the support of the Ministry of Science and Higher Education of Russia, grant № (075-15-2021-671).

Conflict of interest: The authors declare no conflicts of interest.

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