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Thermodynamic and thermochemical properties of $Cu_3(PO_4)_2·3H_2O$

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Copper (II) orthophosphate trihydrate $Cu_3(PO_4)_2·3H_2O$ has been synthesized by the exchange chemical reactions in aqueous solutions from the compounds $Cu(NO_3)_2·3H_2O$, NH_4OH and H_3PO_4. The final product has been investigated by using atomic absorption spectroscopy (AAS), infrared spectrometry (IRS), differential thermal analysis (DTA) and X-ray powder diffraction (XRD) techniques. For the first time, the experimental heat capacity C_p° of $Cu_3(PO_4)_2·3H_2O$ has been investigated in the temperature range 198–402 K. Combining the experimental results with the literature data made it possible to determine the thermodynamic and thermochemical properties, such as enthalpy H_T°, entropy S_T°, Gibbs energy G_T°, enthalpy of formation $\Delta H_{f(T)}^\circ$, Gibbs energy of formation $\Delta G_{f(T)}^\circ$ and logarithm of the equilibrium constant of formation reaction $\log[K_{f(T)}^\circ]$, for the title compound. It was found that at the extreme temperatures of the experiment, $Cu_3(PO_4)_2·3H_2O$ has $C_p^\circ = 245.96$ J·mol^{-1}·K^{-1}, $H^\circ = -3169.59$ kJ·mol^{-1}, $S^\circ = 311.34$ J·mol^{-1}·K^{-1}, $G^\circ = -3231.24$ kJ·mol^{-1} (at 198 K); $C_p^\circ = 455.31$ J·mol^{-1}·K^{-1}, $H^\circ = -3097.93$ kJ·mol^{-1}, $S^\circ = 551.48$ J·mol^{-1}·K^{-1}, $G^\circ = -3319.62$ kJ·mol^{-1}, $\Delta H_f^\circ = -3138.48$ kJ·mol^{-1}, $\Delta G_f^\circ = -2625.39$ kJ·mol^{-1}, $\log[K_f^\circ] = 341.13$ (at 402 K).

Keywords: copper (II) orthophosphate trihydrate, isobaric heat capacity, thermodynamic and thermochemical functions

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INTRODUCTION

In the past few years, copper (II) orthophosphate trihydrate $Cu_3(PO_4)_2{\cdot}3H_2O$ has gained a significant increase of the scientific interest. Thus, a number of promising composites have been obtained with the participation of this compound: a colorimetric platform for glucose detection [1], a colorimetric biosensor for epinephrine identification [2], a nanomaterial for pyruvate specification in fermentation processes [3], a catalyst for olive oil hydrolysis [4], a surfactant [5], an enzyme immobilizer [6] and a nanocatalyst for the hydrolysis of allergenic cow's milk proteins [7].

At the same time, the basic physicochemical properties of individual $Cu_3(PO_4)_2{\cdot}3H_2O$ have been studied insufficiently. In particular, the thermodynamic and thermochemical parameters of the title compound were determined primarily at the standard conditions and are somewhat controversial (see Table 1).

Almost all of the literature data in Table 1 have been estimated; and only in one study [9], the enthalpy of formation ΔH_f° of $Cu_3(PO_4)_2{\cdot}3H_2O$ was experimentally investigated. However, the result of Ref. [9] is questionable: ΔH_f° is positive (which is rare for solid compounds [15]) and seems to be rather overestimated (Table 1). One may suppose that the authors of [9] made some mistakes in recording the sign and in the units of measurement, because the value –2750.4 (–11507.7/4.184) kJ·mol^{-1} appears be more reliable.

The authors of Ref. [8] tried to predict $C_p^\circ(Cu_3(PO_4)_2{\cdot}3H_2O)$ in the form of the classical Maier–Kelley equation (1) [16] (there was no formula in Ref. [8], but the values of the necessary coefficients were given)

$$C_p^\circ = 226.5 + 0.0297T - 10040000T^{-2}, \quad (1)$$

where T is the absolute temperature.

Here it must be noted that Eq. (1) is sometimes written differently [10] as (2):

$$C_p^\circ = 226.5 + 0.0297T + 10040000T^{-2}. \quad (2)$$

However, expressions (v) and (2) have significant drawbacks. Thus, according to Eq. (1), the heat capacity increases monotonically with temperature, but $C_p^\circ(Cu_3(PO_4)_2{\cdot}3H_2O)$ is almost three times lower than the other data [11, 13]. Furthermore, according to Eq. (2), the heat capacity of this crystalline phosphate is 348.4 J·mol^{-1}·K^{-1} at 298 K (Table 1). In this case, the result of Ref. [8] will differ slightly from the later data [11, 13]. However, as the temperature rises from 299 to 874 K, the heat capacity will only decrease, which makes no physical and physicochemical senses.

As can be seen, the main drawback of the publications on $Cu_3(PO_4)_2{\cdot}3H_2O$ is the lack of experimental data on the heat capacity in wide temperature ranges. This lack also makes it impossible to reliably determine the temperature dependences of other thermodynamic (enthalpy H_T°, entropy S_T° and Gibbs energy G_T°) and thermochemical (enthalpy of formation $\Delta H_{f(T)}^\circ$, Gibbs energy of formation $\Delta G_{f(T)}^\circ$ and the logarithm of the equilibrium constant of formation reaction $\log[K_{f(T)}^\circ]$) functions for this compound.

Given the above problems, the aim of this work was to experimentally study the temperature dependence of the heat capacity and to determine the basic thermodynamic and thermochemical parameters for $Cu_3(PO_4)_2{\cdot}3H_2O$.

EXPERIMENTAL

The sample of copper (II) orthophosphate trihydrate $Cu_3(PO_4)_2{\cdot}3H_2O$ was synthesized by

Table 1. **Literature data on the thermodynamic and thermochemical properties of $Cu_3(PO_4)_2{\cdot}3H_2O$ at 298 K**

C_p°, J·mol^{-1}·K^{-1}	S°, J·mol^{-1}·K^{-1}	ΔH_f°, kJ·mol^{-1}	ΔG_f°, kJ·mol^{-1}	Source
348.4	386.8	–3303.0	–2918.4	Maslikova and Chemodanov (1972) [8]
–	–	11507.7*	–	Volkov et al. (1975) [9]
–	–	–3139.70	–2753.05	Vieillard and Tardy (1984) [10]
351	504	–	–2767.75	Puigdomenech and Taxén (2000) [11]
–	–	–3139.83	–2762.24	La Iglesia (2009) [12]
333	–	–	–	Magnusson and Frisk (2014) [13]

Note: * The original ΔH_f° value was reported in kkal·mol^{-1}; here this value is converted to kJ·mol^{-1} (1 kal = 4.184 J [14]) for the sake of consistency.

the exchange reactions from aqueous solutions. $Cu(NO_3)_2{\cdot}3H_2O$, NH_4OH and H_3PO_4 were used for this purpose. The synthesis method for obtaining $Cu_3(PO_4)_2{\cdot}3H_2O$ was developed at the Department of Physical and Colloid Chemistry of Uzhhorod National University. The methods of the synthesis of divalent metal orthophosphates described in Refs. [17, 18] were used as a basis.

The copper content in the final product was monitored by atomic absorption spectroscopy (AAS). For this purpose, an Aurora Instruments spectrometer (AI 1200 GFAAS [19]) was used. A small part of the synthesized copper (II) orthophosphate trihydrate was dissolved in HNO_3. The sample was injected into a graphite furnace and atomized by electrothermal analysis. The maximum process temperature reached 2573 K. The light from a hollow copper cathode lamp was passed through the atomized vapour. The monochromator was adjusted to the wavelength $\lambda = 324.8$ nm (Cu analytical line). The amount of copper was determined by using the method of a calibration graph on the absorption versus concentration.

The infrared (IR) spectra of $Cu_3(PO_4)_2{\cdot}3H_2O$ were recorded on a JASCO Fourier Transform/Infrared-4700 spectrometer. For this purpose, we used the method of attenuated total reflectance (ATR). The corresponding spectra were recorded in the range 4000–400 cm^{-1} using the MIRacle PIKE Accessory [20]. The IR spectra were identified according to the recommendations [21].

The differential thermal analysis (DTA) was performed according to the classical method [22]. The substance in open quartz vessels was heated at a rate of 10 K/min from room temperature to 843–1123 K. The signal from the thermocouples was recorded and processed by a personal computer (PC).

The X-ray diffraction (XRD) analysis was carried out based on the experimental theoretically calculated diffractograms. The experimental diffractograms were obtained using a conventional Bragg-Brentano powder diffractometer (Ni-filtered CuKα radiation with $\lambda = 0.1541$ nm). Indexing of the experimental reflections and the calculation of cell parameters were performed using the PC programs POWDERCELL 2.0 [23] and UNITCELL [24], respectively.

The heat capacity of copper (II) orthophosphate trihydrate was measured using an IT-S-400 device in the temperature range 198–373 K. The sample was cooled to low temperatures using liquid nitrogen. The measurement step was 25 K [25]. The maximum temperature of the study did not exceed 373 K, because at 381 K $Cu_3(PO_4)_2{\cdot}3H_2O$ began to lose the crystallization water and the dehydration products could damage the measuring cell.

RESULTS AND DISCUSSION

Physicochemical analysis of $Cu_3(PO_4)_2{\cdot}3H_2O$

The copper content in the obtained $Cu_3(PO_4)_2{\cdot}3H_2O$ crystallites was checked by the AAS method. The discrepancy between the set and determined amounts did not exceed 0.30 wt.% Cu. For comparison, Klement and Haselbeck [26] prepared copper (II) orthophosphate trihydrate from $CuSO_4{\cdot}5H_2O$ and $(NH_4)_2HPO_4$, and their difference between the calculated and found copper content was 0.26 wt.%.

Most of the absorption bands of the IR spectrum of the synthesized compound (Fig. 1) were in good agreement with the literature data reported by Jing et al. [27] and with the data given in the Supporting Information of the article by Chen et al. [28].

For thermodynamic studies, it was important to determine the stability and temperature limits of $Cu_3(PO_4)_2{\cdot}3H_2O$. The absorption at 3263 and 3021 cm^{-1} (Fig. 1) could indicate different energies of the crystallization water molecules, which was subsequently confirmed by the thermal studies (Fig. 2).

The two endothermic effects at 402 and 674 K (Fig. 2a) probably corresponded to the stepwise dehydration of $Cu_3(PO_4)_2{\cdot}3H_2O$. However, hypothetically, this compound at 402 K could not lose H_2O, but just melt in the crystallization water, so its mass and chemical composition would not change. This hypothesis required some additional verification; for this purpose, the initial sample of $Cu_3(PO_4)_2{\cdot}3H_2O$ was calcined at 402 K for 1 hour and its mass was observed:

$$\underset{\text{434.626 g/mol}}{\overset{\text{0.511 g}}{Cu_3(PO_4)_2\times 3H_2O}}\;\overset{\text{402 K}}{\underset{\text{1 hour}}{}} =$$

$$\underset{\text{420.214 g/mol}}{\overset{\text{0.495 g}}{Cu_3(PO_4)_2\times 2.2H_2O}} + \underset{\text{13.609 g/mol}}{\overset{\text{0.016 g}}{0.8H_2O}}\,. \qquad (3)$$

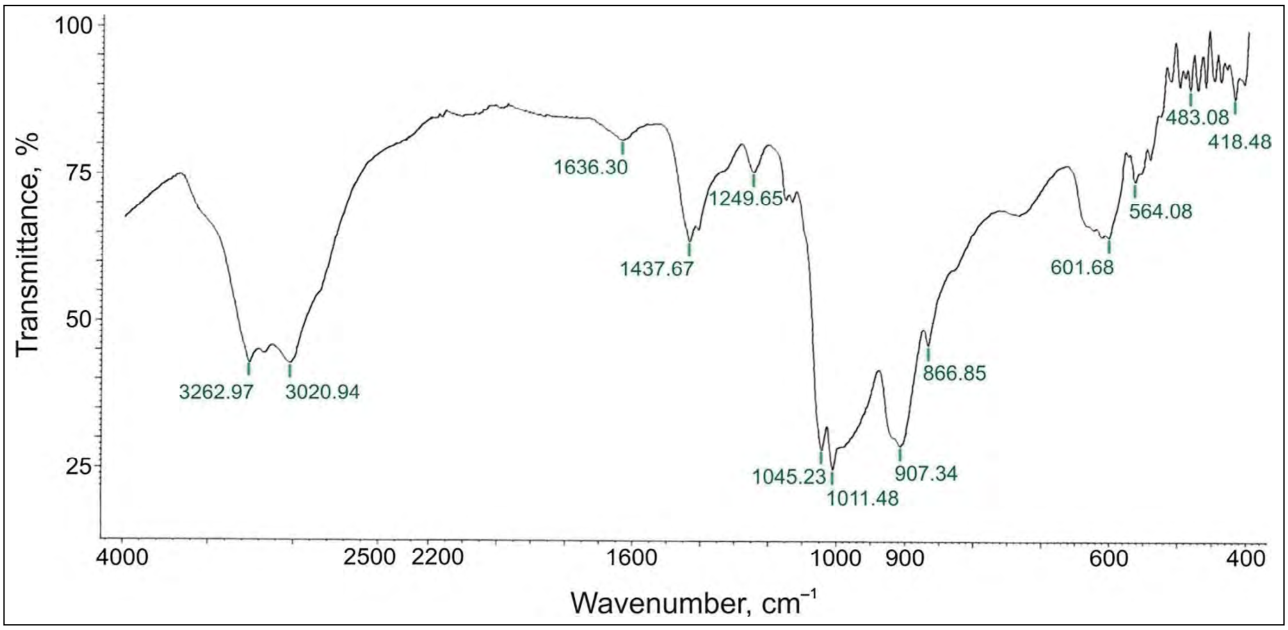

Fig. 1. IR spectrum of synthesized $Cu_3(PO_4)_2{\cdot}3H_2O$

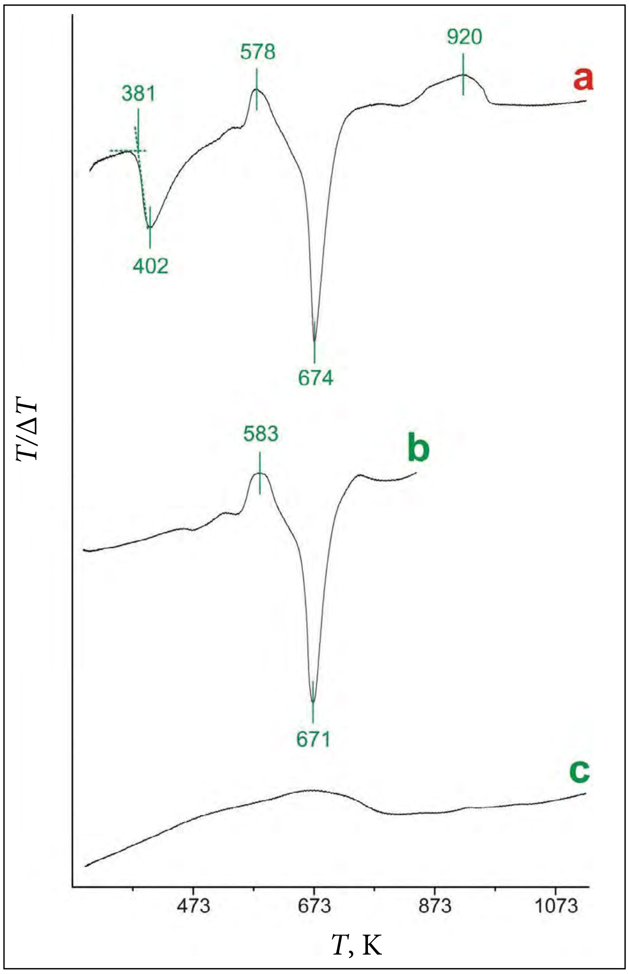

Fig. 2. Heating curves of the synthesized sample: (a) air-dry $Cu_3(PO_4)_2{\cdot}3H_2O$ (Golub et al. [29]); (b) $Cu_3(PO_4)_2{\cdot}3H_2O$ after calcination for 1 hour at 402 K (this work); (c) $Cu_3(PO_4)_2{\cdot}3H_2O$ after calcination for 1 hour at 873 K (this work)

Equation (3) clearly shows that copper (II) orthophosphate trihydrate has lost a mass approaching 1 mole of the crystallization water. The heating curve of such a sample no longer had an end effect at 402 K (Fig. 2b). Thus, $Cu_3(PO_4)_2{\cdot}3H_2O$ exists only up to 402 K. The beginning of the process of loss of the crystallization water can be considered as 381 K temperature (Fig. 2a). Keeping copper (II) orthophosphate trihydrate for 1 hour at 873 K has resulted in the preparation of anhydrous $Cu_3(PO_4)_2$:

$$\underset{434.626\ \text{g/mol}}{\overset{0.478\ \text{g}}{Cu_3(PO_4)_2\times 3H_2O}}\ \underset{1\ \text{hour}}{\overset{873\ \text{K}}{=}}$$

$$\underset{380.580\ \text{g/mol}}{\overset{0.416\ \text{g}}{Cu_3(PO_4)_2}} + \underset{54.046\ \text{g/mol}}{\overset{0.062\ \text{g}}{3H_2O}}\ . \qquad (4)$$

The heating curve of the sample annealed at 873 K no longer had clear thermal effects (Fig. 2c). It is worth noting that the $Cu_3(PO_4)_2{\cdot}3H_2O$ samples before and after heat treatment had different diffractograms (Fig. 3).

The crystal structure of $Cu_3(PO_4)_2{\cdot}3H_2O$ is unknown (Fig. 3a). There is only information [14] that this compound exists in the form of orthorhombic crystallites. Sometimes [27, 28, 31, 32] the JCPD PDF:22-0548, JCPDS:22-0548 or JPSCD00-022-0548 cards are also used, which is actually a standard diffractogram of copper (II) orthophosphate trihydrate (Fig. 3b), but without

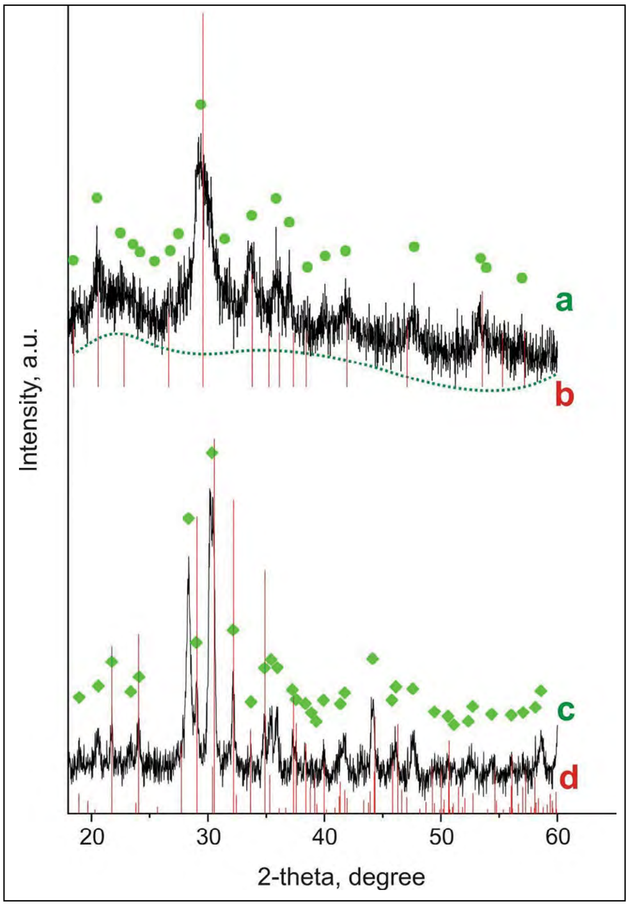

Fig. 3. X-ray diffraction patterns of $Cu_3(PO_4)_2·3H_2O$ and $Cu_3(PO_4)_2$: (a, black lines) air-dry $Cu_3(PO_4)_2·3H_2O$ (Golub et al. [30]); (b, red lines) standard $Cu_3(PO_4)_2·3H_2O$ (by JPSCD00-022-0548, similar to those published in Refs. [27, 28] and given in the Supporting Information to the articles [31, 32]); (c, black lines) $Cu_3(PO_4)_2·3H_2O$ after calcination for 1 hour at 873 K (this work); (d, red lines) anhydrous $Cu_3(PO_4)_2$ (data by Shoemaker et al. [33])

hkl values. The absence of these and other structural data makes it impossible to calculate the parameters of the $Cu_3(PO_4)_2·3H_2O$ unit cell. Therefore, here we will limit ourselves to recording the main reflections of this crystallohydrate (Table 2). Ball [34] did the same for $Cu_3(PO_4)_2$ when the structure of the anhydrous analog was not yet known. Note that most of the reflections of copper (II) orthophosphate trihydrate in Table 2 and Fig. 3a are in good agreement (with deviations within 2θ = 0.03–0.30°) with the values of JPSCD00-022-0548 (Fig. 3b).

The main reflections of $Cu_3(PO_4)_2·3H_2O$ after calcination at 873 K were in good agreement with the X-ray data of Shoemaker et al. [33] for anhydrous $Cu_3(PO_4)_2$ (Fig. 3c, d). This allowed us to index the corresponding diffractogram (Table 3).

According to the data in Table 3, the parameters of the $Cu_3(PO_4)_2$ unit cell (triclinic crystal system) were calculated as follows: a = 0.4857 nm, b = 0.5292 nm, c = 0.6159 nm, α = 72.48°, β = 87.02°, γ = 68.46° and $V = 0.1401\ nm^3$. Let us compare these values with the results of Shoemaker et al. [33]: a = 0.4853 nm, b = 0.5285 nm, c = 0.6182 nm, α = 72.35°, β = 86.99°, γ = 68.54° and $V = 0.1403\ nm^3$. As could be seen, the minimum difference between the parameters of this work and those published in the literature [33] is 0.03%, and the maximum is 0.37%. The differences in the results can be explained by the different methods used to prepare $Cu_3(PO_4)_2$: Shoemaker et al. [33] used CuO, $(NH_4)_2HPO_4$, H_3PO_4 (as starting components) and a high hydrothermal pressure ~2758 bar. It should also be noted that in the literature, even greater differences in the crystal structure parameters of the same compound could be found. For example, the difference between the unit cell parameters of copper (II) pyrophosphate α-$Cu_2P_2O_7$ (also copper-containing phosphate) is close to 0.45%, as can be seen from the comparison of data from Refs. [35] and [36].

Thermodynamic properties of $Cu_3(PO_4)_2·3H_2O$

The analyses confirmed the individuality and stability of the $Cu_3(PO_4)_2·3H_2O$ compound up to temperatures 381–402 K. This allowed us to carry out the following thermodynamic studies. The experimental results of the measured heat capacity of copper (II) orthophosphate trihydrate were

Table 2. **X-ray diffraction data of $Cu_3(PO_4)_2·3H_2O$ in the interval 2θ = (18÷60)°**

2θ, °	I, a.u.	2θ, °	I, a.u.	2θ, °	I, a.u.	2θ, °	I, a.u.
18.43	3	25.42	3	33.75	5	41.80	4
20.46	5	26.76	3	35.83	6	47.70	4
22.48	3	27.47	4	36.97	4	53.41	4
23.56	3	29.39	10	38.54	3	53.86	3
24.17	3	31.43	4	40.06	3	56.95	3

Table 3. **Indexing of the $Cu_3(PO_4)_2$ diffractogram ($Cu_3(PO_4)_2 \cdot 3H_2O$ after calcination at 873 K for 1 hour)**

h k l	2θ, °	2θ, °	h k l	2θ, °	2θ, °
By Shoemaker et al. [33]		This work	By Shoemaker et al. [33]		This work
0 1 0	18.93	18.94	2 0 0	39.97	39.92
0 1 1	20.30	20.59	−1−1 2	41.36	41.37
1 1 0	21.75	21.75	−2−1 1	41.75	41.75
1 1 1	23.80	23.38	2 2 0	44.33	44.20
−1 0 1	24.06	24.09	0−2 1	45.85	45.79
0−1 1	27.72	28.33	0 0 3	46.30	46.13
−1−1 1	29.07	29.00	1 1 3	47.07	47.58
0 1 2	30.55	30.35	−2 0 2	49.26	49.44
1−1 0	32.20	32.16	−2 1 1	50.70	50.62
1 1 2	33.66	33.69	−2−1 2	51.06	51.11
1 2 1	34.88	34.85	1 0 3	52.06	52.35
−1 0 2	35.31	35.42	2 0 2	52.74	52.72
1 2 0	36.11	35.95	1 3 0	54.64	54.35
2 1 0	37.35	37.23	0 3 1	56.09	56.04
1 0 2	37.59	37.56	0 −2 2	57.26	57.08
0 2 0	38.41	38.37	2 2 3	58.07	58.11
1−1 1	38.78	38.88	2 3 2	58.36	58.58
2 1 1	39.18	39.29			

plotted against the dependence C_p° = f(T). The resulting curve was almost straightforward (Fig. 4) and can be described by Eq. (5):

$$C_p^\circ = 45.27 + 1.02T. \tag{5}$$

The correlation coefficient R and the coefficient of determination R^2 [37] are 0.999 and 0.998 for dependence (5), respectively.

As shown above, the formula unit of $Cu_3(PO_4)_2 \cdot 3H_2O$ loses 1 molecule of crystallization water

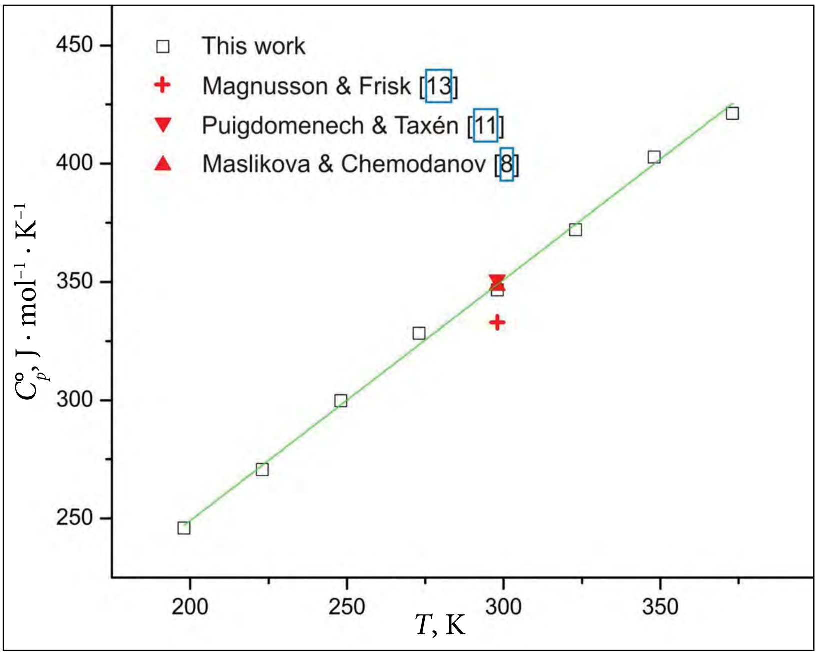

Fig. 4. Dependence of the isobaric heat capacity on temperature for $Cu_3(PO_4)_2 \cdot 3H_2O$

at 402 K. This temperature was considered to be the extreme temperature at which copper (II) orthophosphate trihydrate could still exist. Therefore, the values of C°_p in the interval 373–402 K were estimated by extrapolating the found dependence (5). This approach does not contradict the classical ideas [15]: for the most part, the heat capacity curve of solids retains its course when approaching the first phase transformation or even the decomposition temperature (the temperature limit of the compound existence).

The thermodynamic functions for copper (II) orthophosphate trihydrate were determined according to the rules of chemical thermodynamics [15, 38]. The total enthalpy was calculated by expressions (6) and (7)

$$H^\circ_T = \Delta H^\circ_f(298) + (H^\circ_{T\max} - H^\circ_{298}) - (H^\circ_{298} - H^\circ_{T\min}), \quad (6)$$

$$H^\circ_T = \Delta H^\circ_{f(298)} + \int_{298}^{T_{\max}} C^\circ_p dT - \int_{T_{\min}}^{298} C^\circ_p dT, \quad (7)$$

where $T_{\min}$ = 198–298 K and $T_{\max}$ = 298–402 K.

The most accurate value was considered to be $\Delta H^\circ_{f(298)}(Cu_3(PO_4)_2{\cdot}3H_2O)$ = –3139.77 kJ·mol^{-1}. This value is an average of the data of Refs. [10, 12] (Table 1). The enthalpy increments $H^\circ_{298} - H^\circ_{T\min}$ and $H^\circ_{T\max} - H^\circ_{298}$ were found by integrating equation (5). The obtained dependence $H_T = f(T)$ is shown in Fig. 5.

The entropy was determined by formula (8) [15]:

$$S^\circ_T = S^\circ_{298} + \int_{298}^{T_{\max}} \frac{C^\circ_p}{T} dT - \int_{T_{\min}}^{298} \frac{C^\circ_p}{T} dT. \quad (8)$$

The literature data reported for $S^\circ_{298}(Cu_3(PO_4)_2{\cdot}3H_2O)$ are very different from each other [8, 11] (Table 1). This made it impossible to use their average value. Therefore, we made the alternative calculations using the classical expressions (9) and (10) [15, 38]:

$$S^\circ_{298} = (H^\circ_{298} - G^\circ_{298})/298, \quad (9)$$

$$G^\circ_{298}\text{(compound)} = \Delta G^\circ_{f(298)}\text{(compound)} + $$

$$+ \Sigma G^\circ_{298}\text{ (elemental components)}. \quad (10)$$

The value of $\Delta G^\circ_{f(298)}(Cu_3(PO_4)_2{\cdot}3H_2O)$ causes the least controversy. The almost identical values were obtained in three different works [10–12] (the maximum difference does not exceed 0.53%). Therefore, the value –2761.01 kJ·mol^{-1}, which is the average of the data given in Refs. [10–12], was considered to be true (Table 1). To calculate $G^\circ_{298}(Cu_3(PO_4)_2{\cdot}3H_2O)$, we also used G°_{298}(Cu),

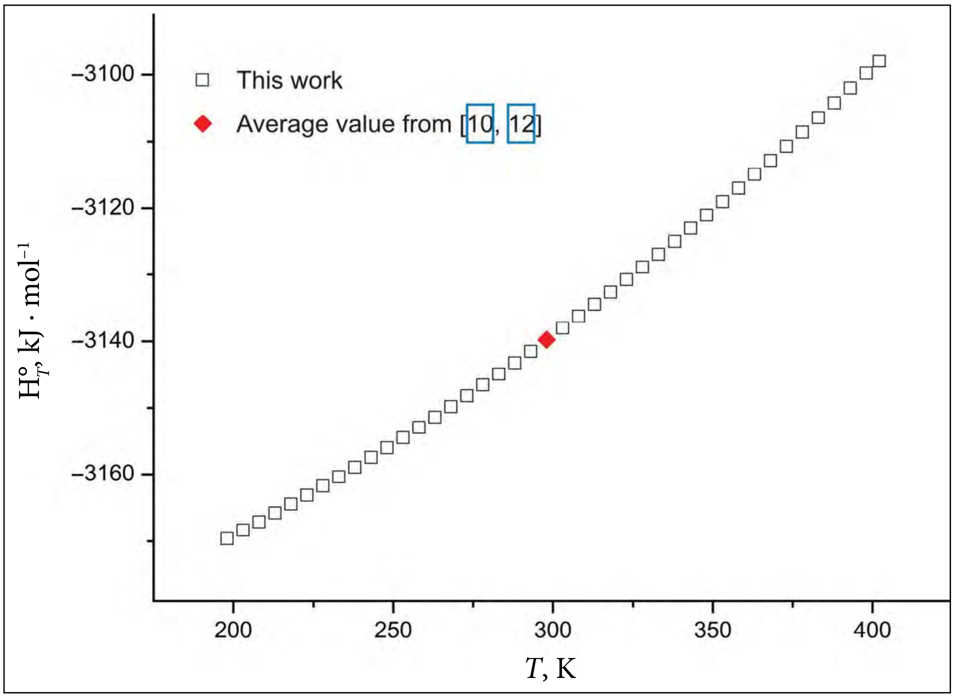

Fig. 5. Dependence of the enthalpy on temperature for $Cu_3(PO_4)_2{\cdot}3H_2O$

G°_{298}(P), $G^\circ_{298}(O_2)$ and $G^\circ_{298}(H_2)$ from Ref. [15]. The value of $S^\circ_{298}(Cu_3(PO_4)_2\cdot 3H_2O)$ was found to be 431.85 J·mol^{-1}·K^{-1}. The combination of Eqs. (5) and (8) made it possible to determine $S^\circ_T = f(T)$ for copper (II) orthophosphate trihydrate (Fig. 6).

The determined temperature dependences of H°_T and S°_T allowed us to find $G^\circ_T(Cu_3(PO_4)_2\cdot 3H_2O)$ using formula (11) (a more general equation of expression (9)):

$$G^\circ_T = H^\circ_T - TS^\circ_T. \quad (11)$$

The resulting $G^\circ_T = f(T)$ dependence is shown in Fig. 7.

It is interesting to compare the experimental (obtained on the basis of our C°_p data) temperature dependence of $G^\circ_T(Cu_3(PO_4)_2\cdot 3H_2O)$ with the calculated one (using the modern Magnusson-Frisk method (MFM) [13]). To do this, consider Fig. 7 and Table 4.

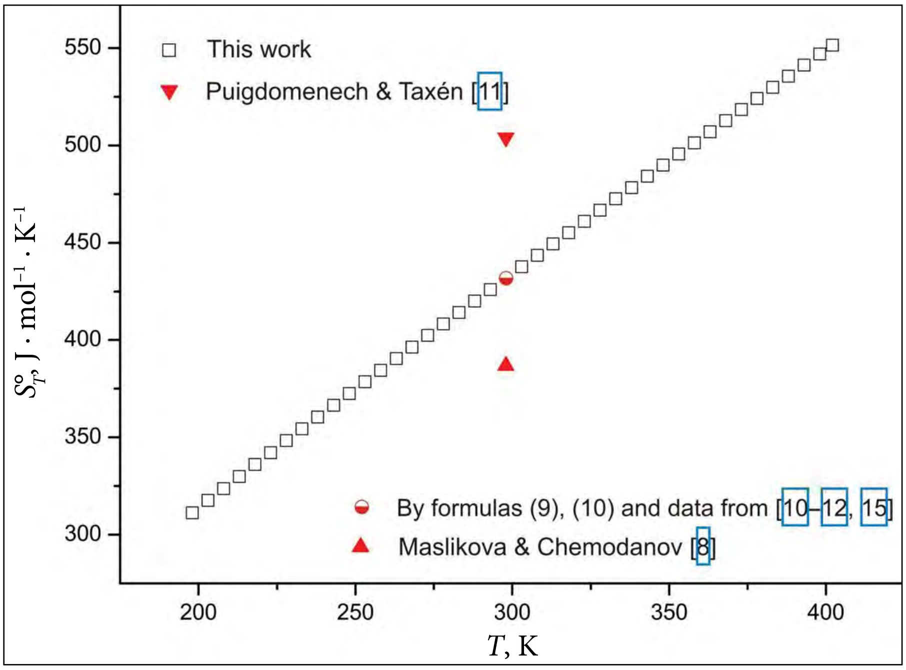

Fig. 6. Dependence of the entropy on temperature for $Cu_3(PO_4)_2\cdot 3H_2O$

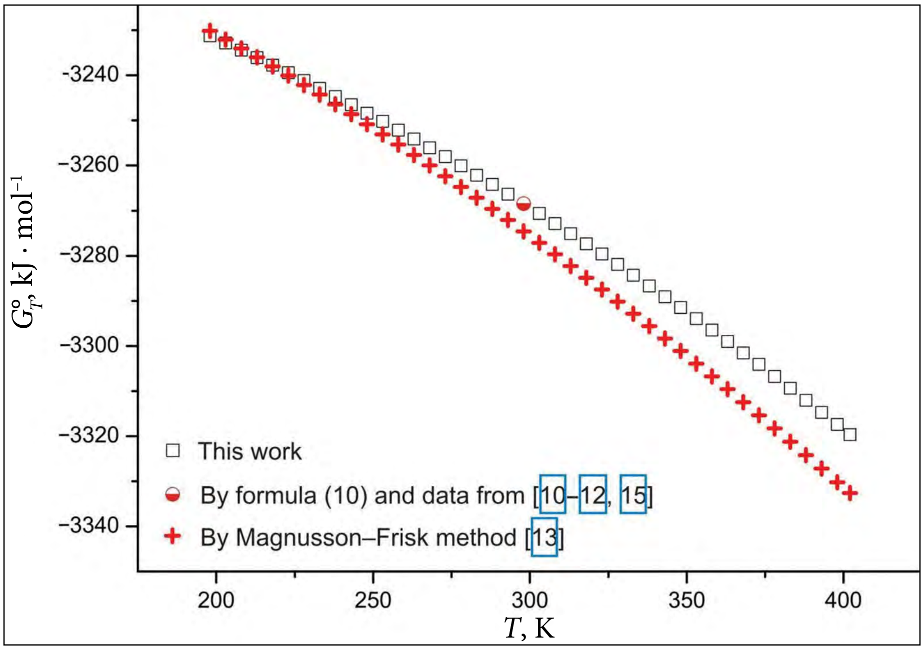

Fig. 7. Dependence of the Gibbs energy on temperature for $Cu_3(PO_4)_2\cdot 3H_2O$

Table 4. **Comparison of the values of $G^\circ_T(Cu_3(PO_4)_2{\cdot}3H_2O)$ of the present work with those calculated by the Magnusson–Frisk method**

T, K	This work, kJ·mol^{-1}	MFM, kJ·mol^{-1}	Δ, %	*T*, K	This work, kJ·mol^{-1}	MFM, kJ·mol^{-1}	Δ, %
198	–3231.24	–3230.14	–0.03	300	–3269.33	–3275.58	0.19
200	–3231.87	–3230.91	–0.03	310	–3273.73	–3280.70	0.21
210	–3235.06	–3234.81	–0.01	320	–3278.24	–3285.92	0.23
220	–3238.39	–3238.85	0.01	330	–3282.88	–3291.25	0.25
230	–3241.83	–3243.01	0.04	340	–3287.62	–3296.69	0.28
240	–3245.40	–3247.30	0.06	350	–3292.49	–3302.23	0.30
250	–3249.10	–3251.72	0.08	360	–3297.47	–3307.88	0.32
260	–3252.90	–3256.25	0.10	370	–3302.56	–3313.62	0.33
270	–3256.83	–3260.91	0.13	380	–3307.77	–3319.46	0.35
273	–3258.03	–3262.33	0.13	390	–3313.09	–3325.40	0.37
280	–3260.88	–3265.68	0.15	400	–3318.53	–3331.43	0.39
290	–3265.04	–3270.58	0.17	402	–3319.62	–3332.65	0.39

As can be seen from Table 4, in the low temperature range 198–273 K, the differences in the results are close to 0.1%. With increasing temperature, the difference between the experiment and the calculation increases slightly, but does not exceed 0.4%. Thus, the theoretical Magnusson-Frisk equation (12) [13],

$$G^\circ_T = -3237200 + 1632.9T - 306.27T\ln T - 0.11081T^2 + 1737500T^{-1}, \qquad (12)$$

is in good agreement with our experiment. Expression (12) describes the temperature dependence of the Gibbs energy for $Cu_3(PO_4)_2{\cdot}3H_2O$ with a sufficient accuracy.

Thermochemical properties of $Cu_3(PO_4)_2{\cdot}3H_2O$

In the literature, it was not possible to find the values of the thermodynamic functions for elementary components at low temperatures <298 K. Therefore, the calculations of the thermochemical parameters $\Delta\ H^\circ_f$, $\Delta\ G^\circ_f$ and $\log[K^\circ_f]$ for $Cu_3(PO_4)_2{\cdot}3H_2O$ were performed only for temperatures >298 K.

The known values of H°_T and G°_T for Cu, P (white modification), O_2 and H_2 were taken from the reference book [15]. The temperature dependences of these functions for the interval 298–500 K were described by interpolation equations with $R^2 = 0.997–1.000$; this made it possible to find the values of H°_T and G°_T with a high accuracy every 5 K in the range 300–402 K. The temperature dependence of the enthalpy of the formation of copper (II) orthophosphate trihydrate was determined by Eq. (13) (expression (10) adapted to H°_T):

$$\Delta H^\circ_{f(T)}(Cu_3(PO_4)_2\cdot 3H_2O) = \Delta H^\circ_{(T)}(Cu_3(PO_4)_2\cdot 3H_2O) - \Sigma[3H^\circ_{(T)}(Cu) + 2H^\circ_T(P) + 5.5H^\circ_T(O_2) + 3H^\circ_T(H_2)]. \qquad (13)$$

The values of H°_T $(Cu_3(PO_4)_2{\cdot}3H_2O)$ were taken from Fig. 5. The obtained dependence $\Delta H^\circ_{f(T)\,)} = f(T)$ is shown in Fig. 8.

The temperature dependence of the Gibbs energy of the formation of copper (II) orthophosphate trihydrate was determined by Eq. (14) (expression (10) adapted to this compound):

$$\Delta G^\circ_{f(T)}(Cu_3(PO_4)_2\cdot 3H_2O) = \Delta G^\circ_{(T)}(Cu_3(PO_4)_2\cdot 3H_2O) - \Sigma[3G^\circ_{(T)}(Cu) + 2G^\circ_T(P) + 5.5G^\circ_T(O_2) + 3G^\circ_T(H_2)]. \qquad (14)$$

The values of G°_T $(Cu_3(PO_4)_2{\cdot}3H_2O)$ were taken from Fig. 7. The obtained dependence $\Delta G^\circ_{f(T)} = f(T)$ is shown in Fig. 9.

Let us compare the experimental (obtained on the basis of our C°_p data) temperature dependence of $\Delta G^\circ_{f(T)}(Cu_3(PO_4)_2{\cdot}3H_2O)$ with the calculated one (using the Chermak-Rimstidt method (ChRM) [39]). To do this, consider Fig. 9 and Table 5.

As can be seen from Table 5, the maximum differences between the experiment and the calculation do not exceed 0.31%. It was found that the Chermak-Rimstidt expression (15) [12, 39],

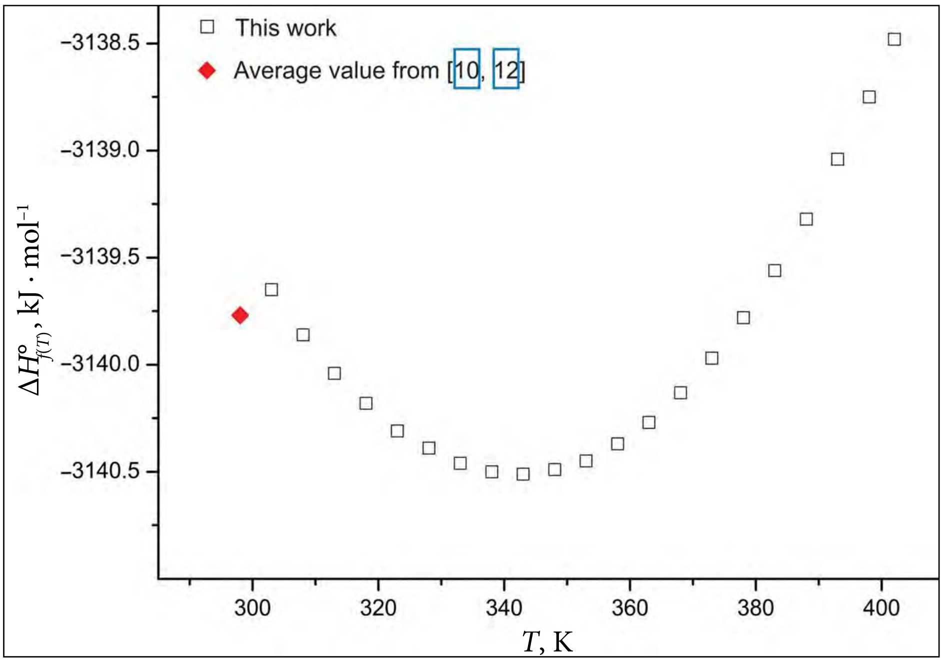

Fig. 8. Dependence of the enthalpy of formation on temperature for $Cu_3(PO_4)_2{\cdot}3H_2O$

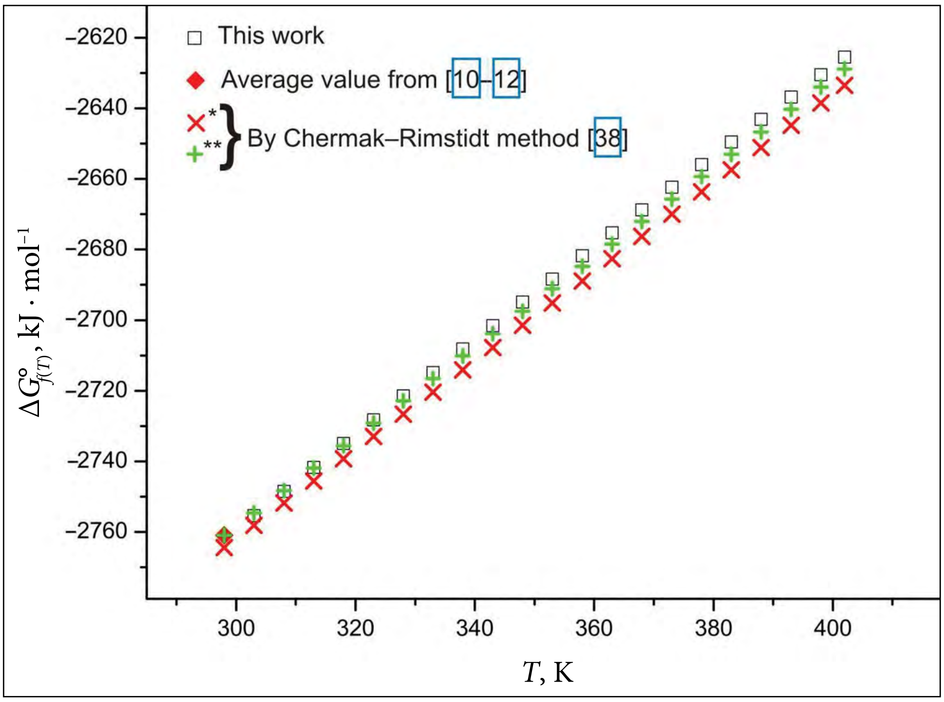

Fig. 9. Dependence of the Gibbs energy of formation on temperature for $Cu_3(PO_4)_2{\cdot}3H_2O$ (see notes to Table 5 for explanation of * and ** symbols)

$$\Delta G^\circ_{f(T)} = -\Delta H^\circ_{f(298)} - [T(\Delta H^\circ_{f(298)} - \Delta G^\circ_{f(298)})]/298, \quad (15)$$

is in the best agreement with the experimental results if we use $\Delta G^\circ_{f(298)}$ and $\Delta H^\circ_{f(298)}$ of the final product $Cu_3(PO_4)_2{\cdot}3H_2O$, rather than the polyhedral components CuO, P_2O_5 and $H_2O_{(cryst)}$. As a result, the maximum deviation of the calculated curve $\Delta G^\circ_{f(T)} = f(T)$ from the experiment can be reduced to 0.13% (Table 5, Fig. 9).

For reaction (16)

$$3Cu + 2P + 5.5O_2 + 3H_2 = Cu_3(PO_4)_2 \cdot 3H_2O, \quad (16)$$

Table 5. **Comparison of the values of $\Delta G^\circ_f(Cu_3(PO_4)_2 \cdot 3H_2O)$ in this work with those calculated by the Chermak–Rimstidt method**

T, K	This work, kJ·mol^{-1}	ChRM *, kJ·mol^{-1}	Δ, %	ChRM **, kJ·mol^{-1}	Δ, %
300	–2759.51	–2761.96	0.09	–2758.47	–0.04
310	–2745.85	–2749.36	0.13	–2745.76	< –0.01
320	–2732.26	–2736.76	0.16	–2733.05	0.03
330	–2718.83	–2724.16	0.20	–2720.34	0.06
340	–2705.48	–2711.56	0.22	–2707.63	0.08
350	–2692.28	–2698.96	0.25	–2694.92	0.10
360	–2679.18	–2686.36	0.27	–2682.21	0.11
370	–2666.18	–2673.76	0.28	–2669.50	0.12
380	–2653.32	–2661.16	0.30	–2656.79	0.13
390	–2640.56	–2648.56	0.30	–2644.08	0.13
400	–2627.91	–2635.96	0.31	–2631.37	0.13
402	–2625.39	–2633.44	0.31	–2628.83	0.13

Notes: * values obtained by using $\Delta G^\circ_{f(298)}$ and $\Delta H^\circ_{f(298)}$ for CuO, P_2O_5 and $H_2O_{(cryst)}$ from Ref. [12]; ** values were obtained using $\Delta G^\circ_{f(298)}$ and $\Delta H^\circ_{f(298)}$ for $Cu_3(PO_4)_2 \cdot 3H_2O$, which were selected from Refs. [10–12].

the logarithm of the equilibrium constant of formation reaction $\log[K^\circ_{f(T)}]$ was determined. For this purpose, we used formula (17) [15, 38]:

$$\log[K^\circ_{f(T)}] = -\Delta G^\circ_{f(T)} / (19.1448T). \qquad (17)$$

The obtained temperature dependence of $\log[K^\circ_{f(T)}]$ is shown in Fig. 10.

Thus, the results obtained in this work significantly expand the scientific knowledge of the thermodynamic and thermochemical properties of copper (II) orthophosphate trihydrate. The data obtained can be useful for modelling physicochemical interactions in complex systems containing $Cu_3(PO_4)_2 \cdot 3H_2O$ or for developing new more competitive methods for the synthesis

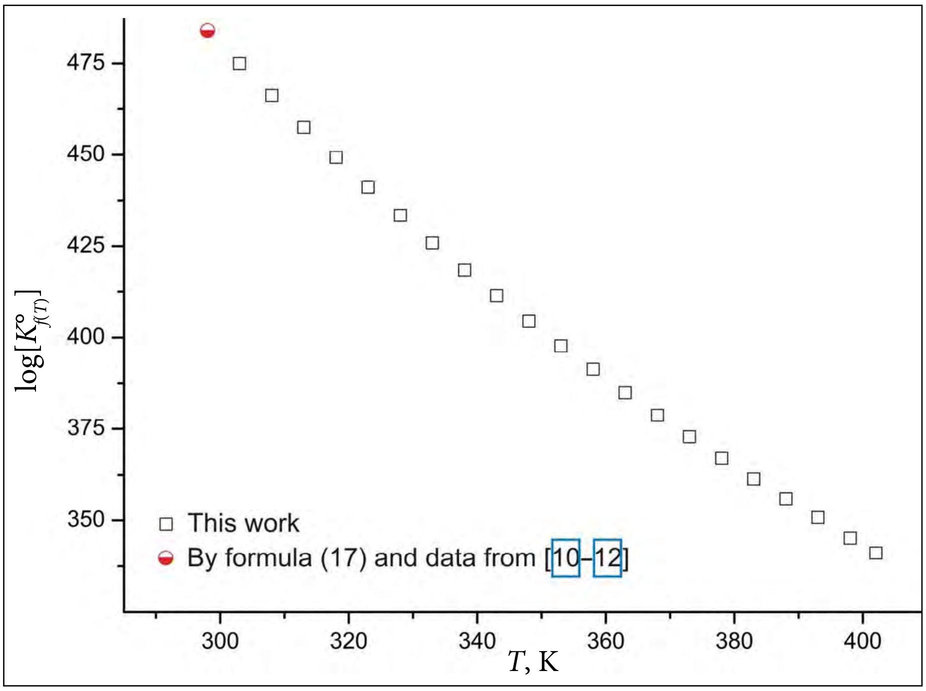

Fig. 10. Dependence of the logarithm of the equilibrium constant of formation reaction from the elemental components on temperature for $Cu_3(PO_4)_2 \cdot 3H_2O$

of this compound. This is especially relevant in view of the promising micro- and nanosystems [1–7, 27, 28, 31, 32] already obtained with the participation of copper (II) orthophosphate trihydrate.

CONCLUSIONS

For the first time, the isobaric heat capacity in the temperature range 198–402 K has been experimentally investigated for $Cu_3(PO_4)_2\cdot3H_2O$. The basic thermodynamic (at 198–402 K) and thermochemical (at 298–402 K) functions of this compound have been determined. It was found that for copper (II) orthophosphate trihydrate, some methods for predicting the total Gibbs energy and the Gibbs energy of formation are in good agreement (with the errors of 0.1–0.4%) with the experimental results.

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$Cu_3(PO_4)_2 \cdot 3H_2O$ TERMODINAMINĖS IR TERMOCHEMINĖS SAVYBĖS

Santrauka

Vario (II) ortofosfato trihidratas $Cu_3(PO_4)_2 \cdot 3H_2O$ buvo susintetintas vandeninėje terpėje iš $Cu(NO_3)_2 \cdot 3H_2O$, NH_4OH ir H_3PO_4. Gautas produktas ištirtas panaudojus atominę absorbcinę spektroskopiją (AAS), infraraudonąją spektroskopiją, diferencinę terminę analizę ir Rentgeno spindulių difrakciją. Eksperimentiškai buvo pirmą kartą nustatyta $Cu_3(PO_4)_2 \cdot 3H_2O$ šilumos talpa 198–402 K temperatūros ruože, taip pat nustatytos pagrindinės termodinaminės ir termocheminės savybės.