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Influence of temperature on the hydration equilibria and phase transitions.

III. Quantitative description of the cooling curve obtained on the basis of polythermal crystallization of $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ from water

Wpływ temperatury na równowagi i przemiany hydratacyjne.

III. Ilościowy opis krzywej ochładzania na podstawie politermicznej krystalizacji $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ z wody

1. INTRODUCTION

The undertaken investigations are an attempt at adaptation of cooling curves obtained from polythermal crystallization for recognition of energetical aspect of hydration transitions in variable temperature conditions. The difficulties in description of such process are connected not only with thermokinetics [1] but also with different chemical factors resulting from low-energy equilibria and hydration transitions in concentrated solutions and in formed crystalline phase [2]. In such cases the properties of the system are expressed as a function of one variable [3] or described by means of partial differential equations [4]. Our earlier investigations show that numerical differentiation of precisely registered temperature changes taking place during polythermal crystallization [5] and dissolution [6] permits to distinguish the cyclically repeating changes and to ascribe to these changes the character of individual thermal processes. In the investigations described here there were made efforts of mathematical description of cooling curve and then on the basis of third derivative there was made the quantitative analysis of initial thermal cycles represented by this curve.

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2. EXPERIMENTAL

Praseodymium oxide of purity of 99% (CeO_2 ~0.3%, Nd_2O_3 ~0.2%, $\text{La}_2\text{O}_3 < 0.1\%$) was dissolved in 65% analytical grade HNO_3 and mixed in molar ratio of 1 : 2 with an analytical grade NH_4NO_3 (Nitrogen Compounds Factory, Tarnów, Poland). Crystallization with mechanical mixing occurred owing to spontaneous cooling of solution in air. Temperature measurements in the range of 53.0–30.3 °C were performed by means of mercury thermometer with accuracy of 0.1°C. Further crystallization step without the mixing and temperature measurements occurred in temperature range from 30.6 to 17.2°C. 4.84kg of $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ has been obtained with the yield of 73.4%.

Differentiation and numerical interpolation procedures were performed by means of PS-Plot program, and integration procedure – by means of Derive program.

3. RESULTS AND DISCUSSION

The cooling curve obtained during polythermal crystallization of praseodymium-ammonium nitrate from water is presented in Figure 1 (dotted line). Approximation of the cooling curve by the linear curve (thickened curve A_0):

$$T = a + b \cdot t \quad (1)$$

and by the logarithmical curve:

$$T = a \cdot \exp(-b \cdot t) \quad (2)$$

is characterized in Table 1. For linear function the value of a coefficient expresses initial cooling temperature (T_0), and b – coefficient denotes the average cooling rate. In the case of logarithmic function the b coefficient is expressed by reverse proportionality to thermal inertia of the system $[c_p \cdot m]$, where c_p denotes mean specific heat of the system, and m – mass of solution. After appropriate transformations, the linear and logarithmic function will have the following forms:

$$T - T_0 = b \cdot t \quad (3)$$

$$\ln T_0/T = t/c_p \cdot m \quad (4)$$

Table 1. Linear approximation analysis and numerical integration of cooling curve by means of linear (a + b·t) and exponential {a·exp(-b·t)} functions

Analiza aproksymacyjna i całkowanie numeryczne krzywej ochładzania za pomocą funkcji liniowej: a + b·t i wykładniczej: a·exp(-b·t)

Type function	Coefficients of function		C O D*	C _p [deg·g ⁻¹]	Integration	
	a	b			[s]	Σ [deg·s]
A ₀	52.9348	-1.1654E-3	0.9965	–	19164.6	800454.4
E ₀	53.8431	2.8143E-5	0.9937	4.8675	20078.7	825892.0
A ₁	53.0000	-4.3333E-3	1.0000	–	5169.2	216073.8
E ₁	53.0000	8.2780E-5	1.0000	1.6548	6635.5	270657.4

*COD - coefficient of determination

In Figure 1 it has been drawn through two first points of the cooling curve the linear (A₁) and logarithmic (E₁) function, considered as “standard” functions for description of cooling processes of saturated solutions without formation of crystalline phase. At such assumption the temperature region localized between linear (A₀ – A₁) and logarithmic (E₀ – E₁) functions should be formed only by the process of formation and growth of crystalline phase. As it results from Table 1 the linear functions create slightly larger region than logarithmic functions, which is reflected also in average total temperature changes, which are ΣT_L = 30.4927deg for linear and ΣT_E = 27.6500deg for logarithmic function, respectively.

A cooling curve is in its initial (upper) section created by strongly exothermal process of formation of crystalline phase. Description of this section by means of linear and exponential functions strays significantly from its real course. In order to obtain the better description and possibilities of further analysis this section was subjected to interpolation by means of polynomials of A[0] + A[1]X + ... + A[n]Xⁿ for n ranging from 2 to 14, while in Figure 2 there is shown the superposition of individual polynomials. The distinguishing feature of so obtained set of polynomial functions is the behavior of these sets between first and second measuring point, because with the increase of number of interpolation nodes straight line transforms gradually to more and more deep minimum, which attains at 85th second for 15-node polynomial the smallest value (49.78°C). On the basis of obtained polynomials there has been determined the temperature of the system after the first second of the cooling process and then on the basis of equations (3) and (4) there have been calculated the instantaneous cooling rates (dT) and specific heats (c_p) presented in time function in Figure 3.

This nonmonotonic decrease of specific heat as well as the increase of cooling rate of crystallization system in the first second of the process seems unreal. If we assume however, that in the moment of beginning of measurements there occur in saturated solution the endothermal processes connected e.g. with solubilization or structural changes and in addition if we take into account the inaccuracy of measurements resulting from high inertia of mercury thermometer and from long sampling time, then this description will become more probable.

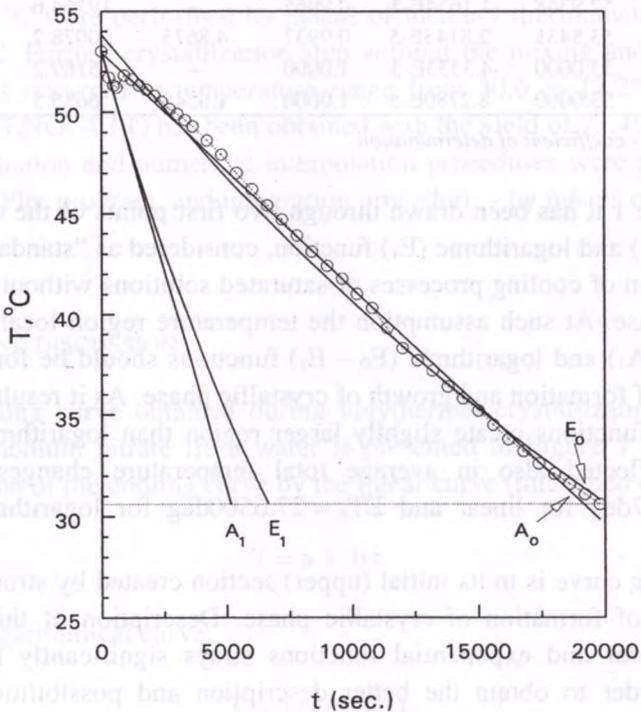


Fig. 1. Cooling curve (dotted line) and approximation linear (A_0) and exponential (E_0) functions.

Linear (A_1) and exponential (E_1) functions were drawn through two initial measuring points of cooling curve in the temperature range from 53.0 to 30.6°C. Krzywa ochładzania (linia przerywana) oraz aproksymacyjna funkcja liniowa (A_0) i wykładnicza (E_0). Funkcję liniową (A_1) i wykładniczą (E_1) przeprowadzono przez dwa początkowe punkty pomiarowe krzywej ochładzania od 53,0 do 30,6°C

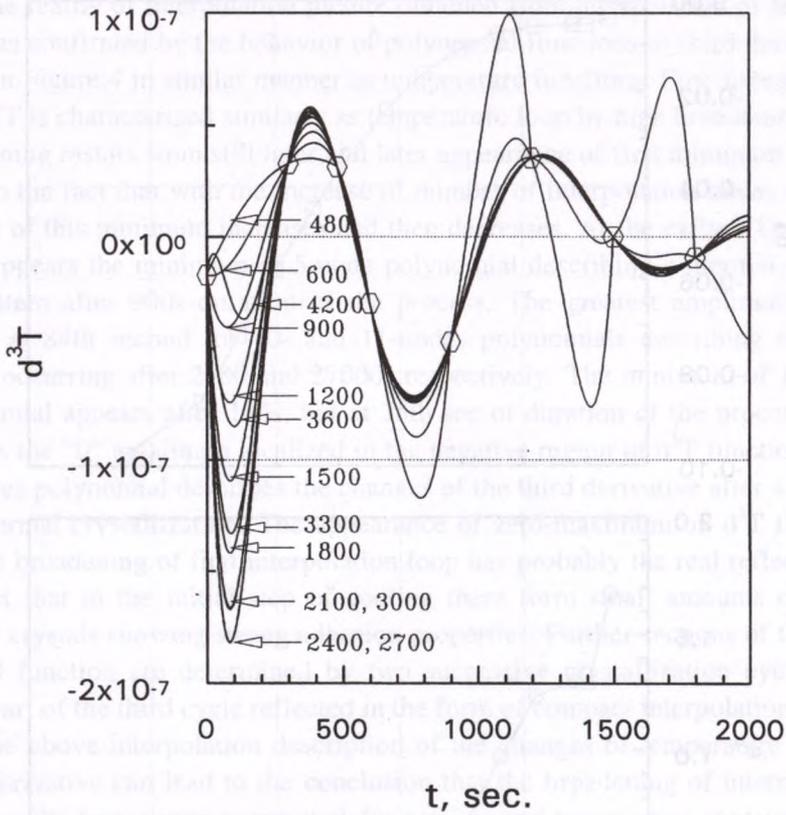


Fig. 2. Interpolation picture of initial section of cooling curve obtained from superposition of polynomials including 3–15 interpolation nodes
 Obraz interpolacyjny początkowego odcinka krzywej ochładzania otrzymany z nałożenia na siebie wielomianów z 3 do 15 węzłami interpolacyjnymi

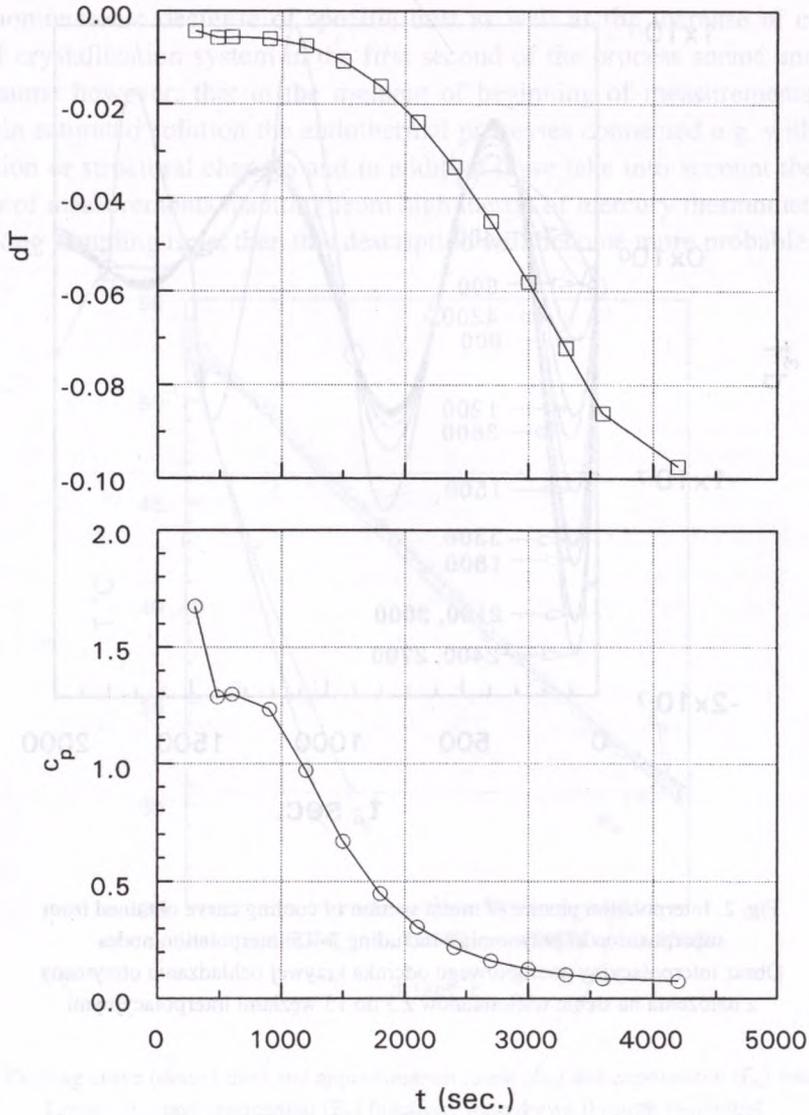


Fig. 3. Changes of first derivative (dT) and specific heat (c_p) in first second of cooling process calculated from equations (3) and (4) and on the basis of temperature changes determined from interpolation of 3–15 initial points of cooling curve by means of polynomials
 Zmiany pierwszej pochodnej (dT) i ciepła właściwego (c_p) w pierwszej sekundzie procesu ochładzania obliczone na podstawie równań (3) i (4) oraz zmian temperatury, otrzymanych z interpolacji wielomianami kolejnych od 3 do 15 początkowych punktów krzywej ochładzania

The reality of interpolation picture obtained from interpolation of temperature was confirmed by the behavior of polynomial functions of third derivatives listed in Figure 4 in similar manner as temperature functions. First interpolation loop d^3T is characterized similarly as temperature loop by high broadening. This broadening results from still later and later appearance of first minimum as well as from the fact that with the increase of number of interpolation nodes the amplitude of this minimum increases and then decreases. At the earliest i.e. at 75s there appears the minimum of 5-node polynomial describing a thermal state of the system after 900s duration of the process. The greatest amplitude is observed at 84th second for 10- and 11-nodes polynomials describing the processes occurring after 2400 and 27000s respectively. The minimum of 15-node polynomial appears after 134s, but at 25th sec of duration of the process there appears the "0" maximum localized in the negative region of d^3T function. This 15-nodes polynomial describes the changes of the third derivative after 4200s of polythermal crystallization. The appearance of zero-maximum on d^3T function and the broadening of first interpolation loop has probably the real reflection in the fact that in the initial step of cooling there form small amounts of good shaped crystals showing strong adhesion properties. Further sections of the considered function are determined by two successive crystallization cycles and some part of the third cycle reflected in the form of compact interpolation loops.

The above interpolation description of the changes of temperature and its third derivative can lead to the conclusion that the broadening of interpolation paths results from errors committed during time and temperature measurements and the course of interpolation function reflects the real behavior of thermal system during polythermal process. In this connection it seems that interpolation of an increasing number of interpolation nodes averages the experimental errors and creates some time perspectives for mathematical picture of polythermal crystallization.

The attempts at quantitative description of individual thermal processes occurring during polythermal crystallization were based on the initial section of 15-nodes d^3T polynomial; the extrema of this polynomial are described by linear functions (Fig. 5). The first linear function is tangent to polynomial in starting point. The parameters of tangent obtained at the height of 0th maximum and the parameters of inflection point (p) determine the second linear function. The parameters of e_1 point localized at the height of first minimum together with parameters of first zero point (a_1) determine the third linear function which combined with the second linear function describe first minimum and determine simultaneously the parameters of e_2 point localized at the height of first maxi-

mum. The parameters of point e_2 combined with the parameters of second zero point (a_2) determine the fourth linear function which together with the third linear function describes first maximum. Transformation of successive linear function realized according to the above procedure, makes possible the description of successive minima and maxima of d^3T function.

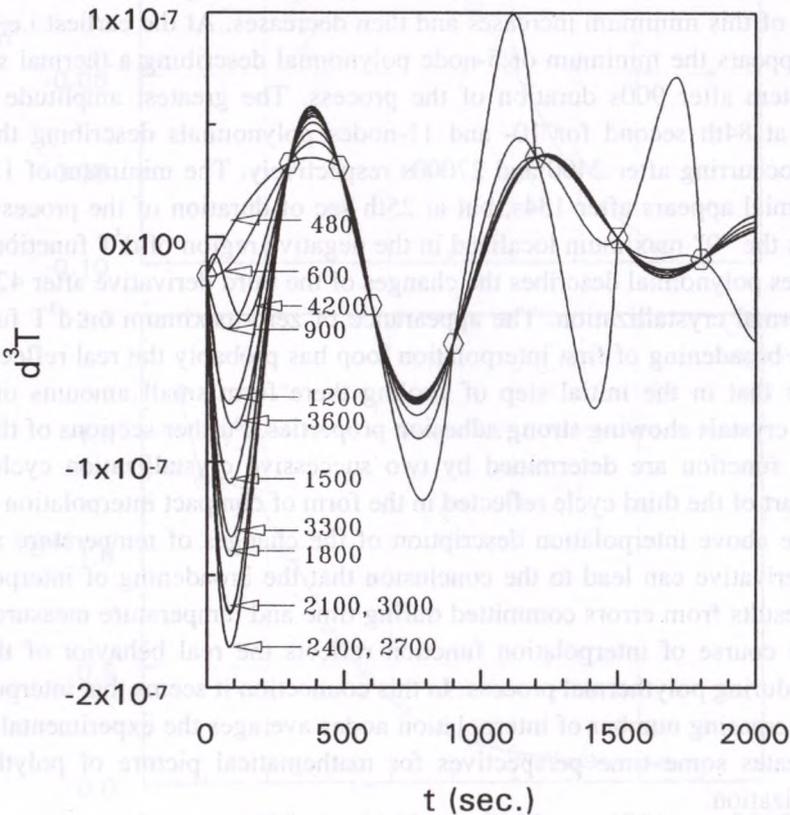


Fig. 4. Initial sections of third derivative (d^3T) of cooling curve obtained from superposition of polynomials including 3–15 interpolation nodes

Początkowe odcinki trzeciej pochodnej (d^3T) krzywej ochładzania, otrzymanej z nałożenia na siebie wielomianów z 3 do 15 węzłami interpolacyjnymi

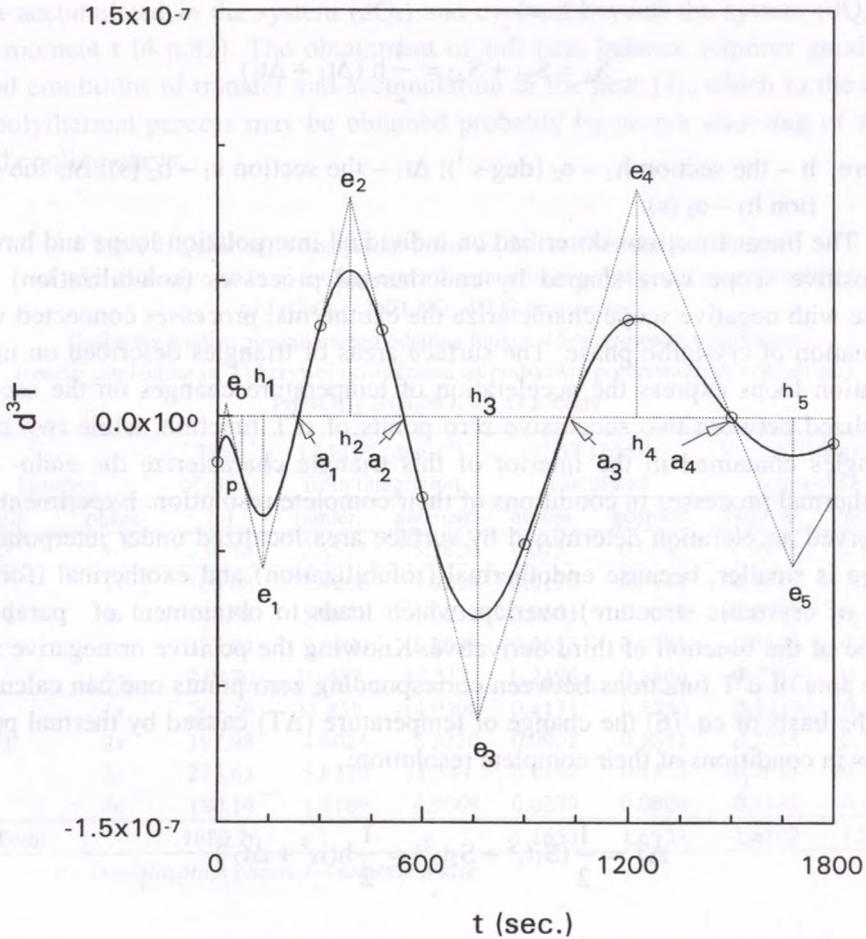


Figure 5. Quantitative analysis of initial section of 15-nodes polynomial of third derivative of cooling curve
 Analiza ilościowa początkowego odcinka 15-węzłowego wielomianu trzeciej pochodnej krzywej ochładzania

Point e_2 obtained from intersection of the third and fourth linear functions represent the vertex of heterolateral triangle, whose base $a_1 - a_2$ is localized on "0" axis of d^3T function, and its height is represented by $h_2 - e_2$ section. Thus the surface area of two adhered right triangles ($S_{\Delta 1}$) and ($S_{\Delta 2}$) may be calculated on the basis of a_1, h_2, a_2 and e_2 parameters:

$$S_{\Delta} = S_{\Delta_1} + S_{\Delta_2} = \frac{1}{2} h (\Delta t_1 + \Delta t_2) \quad (5)$$

where: h – the section $h_2 - e_2$ ($\text{deg} \cdot \text{s}^{-3}$); Δt_1 – the section $a_1 - h_2$ (s); Δt_2 the section $h_2 - a_2$ (s).

The linear functions described on individual interpolation loops and having a positive slope were shaped by endothermal processes (solubilization) and those with negative slope characterize the exothermal processes connected with formation of crystalline phase. The surface areas of triangles described on interpolation loops express the acceleration of temperature changes on the section localized between two successive zero points of d^3T function, while two right triangles contained in the interior of this triangle characterize the endo- and exothermal processes in conditions of their complete resolution. Experimentally observed acceleration determined by surface area localized under interpolation curve is smaller, because endothermal (solubilization) and exothermal (formation of crystalline structure) overlap, which leads to obtainment of parabolic shape of the function of third derivative. Knowing the positive or negative surface area of d^3T functions between corresponding zero points one can calculate on the basis of eq. (6) the change of temperature (ΔT) caused by thermal processes in conditions of their complete resolution:

$$\Delta T = \frac{1}{2} (S_1 t_1^2 + S_2 t_2^2) = \frac{1}{2} h (t_1^3 + \Delta t_2^3) \quad (6)$$

where S denotes the surface area of the phase within the triangle or interpolation loop.

Both steps i.e. endo- and exothermal include each two phases determined by triangles vertices and maxima or minima of interpolation loops. The temperature changes within individual phases were calculated from proportionality of surface area of individual phases to their total surface areas within the endo- or exothermal process. Temperature changes calculated from the functions of third derivative are listed in Table 2 together with the data obtained from direct interpolation of the cooling curve by means of NSpline and polynomial method. The observed differences between the data obtained from the third derivative and those obtained from the cooling curve result from lack of heat balance including the heat evolved during crystallization process (dQ_3) being the sum of

heat accumulated in the system (dQ_1) and evolved beyond the system (dQ_2) at the moment t [4 p.82]. The obtainment of full heat balance requires good defined conditions of transfer and accumulation of the heat [7], which in the case of polythermal process may be obtained probably by proper choosing of standard cooling curve.

Table 2. Quantitative analysis of initial section of 15-nodes polynomial of third derivative (d^3T) of cooling curve obtained from polythermal crystallization of $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ from water

Ilościowa analiza początkowego odcinka funkcji 15-węzłowego wielomianu trzeciej pochodnej (d^3T) krzywej ochładzania na podstawie politermicznej krystalizacji $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ z wody

Number		Time of phase [s]	$ S \cdot 10^{-6}$ [deg·s ⁻²]		$ \Delta T $ [deg]		ΔT [deg]	
cycle	phase		numer.	geometr.	numer.	geometr.	Nspline	Pnomial
0	4c	134.14	2.8523	3.7820	0.0257	0.0340	-0.6472	-2.8314
I	1s	103.68	2.4266	2.9238	0.0130	0.0157	-0.4376	1.2544
	2s	148.69	5.0971	6.0132	0.0563	0.0665	-0.4421	0.1660
	3c	157.04	5.3400	6.3509	0.0658	0.0783	-0.2549	-0.3934
	4c	218.70	10.437	12.317	0.2496	0.2946	-0.2749	0.3452
II	1s	265.26	11.855	-14.9390	0.4171	0.5256	0.3213	0.2717
	2s	197.98	4.6024	8.3220	0.0902	0.1631	-0.2533	-0.2485
	3c	274.63	5.8270	11.544	0.2197	0.4353	-0.2656	-0.2638
	4c	180.14	1.7189	4.9669	0.0279	0.0806	-0.1142	-0.1049
Total		1680.26			1.1653	1.6937	-1.8142	-1.8047

c – crystallization phase, s – solution phase

4. CONCLUSIONS

1. Similarity of description of the cooling curve by linear and exponential function resulted from high thermal inertia of the system. In these conditions the amount of heat evolved from the system is relatively low and linearity of the cooling curve is shaped only by successively repeating cyclic processes of solubilization and crystallization.
2. Use of proper standard curve for making of heat balance of polythermal crystallization may permit to correct the amount of heat liberated to environment.

3. Interpolation of the cooling curve and its higher derivatives by means of polynomials of increasing number of nodes permits to obtain a more detailed picture of behavior of the system especially in initial steps.
4. Numerical integration of third derivative of the cooling curve (d^3T) and inscription of its individual interpolation loops into the triangles permits to describe quantitatively the thermal processes and creates the possibilities of distinguishing of endo- and exothermal processes occurring during polythermal processes.

REFERENCES

- [1] E. K a c k: *Thermokinetics* (in Polish), WNT, Warszawa 1967.
- [2] B. C o n w a y: *Ionic Hydration in Chemistry and Biophysics*, Elsevier, Amsterdam 1981.
- [3] J. D e r e ń, J. H a b e r, R. P a m p u c h: *Solid-State Chemistry* (in Polish), PWN, Warszawa 1975.
- [4] E. K a c k i: *Differential Equations in Physical and Technical Problems* (in Polish), WNT, Warszawa 1995, 44.
- [5] J. H a r k o t: This Vol., Part I.
- [6] J. H a r k o t: This Vol., Part II.
- [7] W. Z i e l e n k i e w i c z, E. M a r g a s: *The Theoretical Principles of Dynamic Calorimetry* (in Polish), Ossolineum, Wrocław 1990.

STRESZCZENIE

Przeprowadzono aproksymację funkcją liniową i wykładniczą krzywej ochładzania, uzyskanej z politermicznej krystalizacji $(\text{NH}_4)_2[\text{Pr}(\text{NO}_3)_5] \cdot 4\text{H}_2\text{O}$ z wody i stwierdzono podobieństwo wykresów obu funkcji. Wskazano na możliwość użycia wzorcowej krzywej ochładzania w celu dokonania bilansu ciepła przenieszonego z układu do otoczenia. Pokazano, że interpolacja wielomianowa krzywej ochładzania, a szczególnie jej trzeciej pochodnej, uszczegółowia obraz termicznego zachowania się układu krystalizacyjnego w początkowym okresie ochładzania, tymczasem numeryczne całkowanie pętli interpolacyjnych trzeciej pochodnej i ich opisanie trójkątami stwarzają możliwość ilościowej analizy cyklicznie powtarzających się procesów rozpuszczania i krystalizacji w procesie politermicznej krystalizacji.