

## **Influence of temperature on the hydration equilibria and phase transitions.**

### **IV. Isothermal dehydration of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$**

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There was performed the isothermal dehydration of hydrated lanthanum nitrate and it was found that apart from temperature and time of heating the shape of dehydration curve was dependent mainly on the amounts of  $\alpha$ - and  $\beta$ - $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  formed in the initial stage of dehydration process. Interpolation of dehydration curves and their third derivatives has permitted to obtain the mass balance of water either for single or for poorly time-resolved hydration-dehydration transitions. There was found the similarity of third derivative functions obtained from stable and unstable dehydration curves, emphasising the similar way of their balancing.

#### 1. INTRODUCTION

Thermodynamic parameters of chemical (material) systems not ensure the obtainment of full picture of their behaviour in dynamic conditions (during the reaction), to which it can testify the example of oscillation reactions [1]. In addition the kinetic investigations made from static positions about kinetic properties of examined system. Therefore the more profound recognitions of different way of utilization (consumption) of potential and kinetic energies [2] being inherent in each chemical (material) object is possible only in these cases when the observed object "is active".

The investigations made by us and relating to the use of third derivative for the examination of rate of temperature change during polythermal crystallization [3] and dissolution [4] create favourable conditions for examination of this phenomenon "in action", because the description of kinetic curves by simple mathematical function transfers the observer in the region of uniform or uni-

formely accelerated (retarded) motion [5]. Owing to this even small and difficult to find by conventional methods non-monotonics in the course of kinetic curves become after triple differentiation strongly intensified and shown (as individual processes) in the form very suitable for its further quantitative and qualitative investigations [3,4,6].

Within this work there was made the analysis of kinetic dehydration curves obtained from isothermal heating of hydrated lanthanum nitrate. In such conditions there is possible the obtainment of more accurate data, than in the case of polythermal crystallization and dissolution.

## 2. EXPERIMENTAL

Lanthanum nitrate synthesized in polythermal conditions and dried at 25 °C until the obtainment of constant mass. Hydration degree of  $\text{La}(\text{NO}_3)_3 \cdot 5.9740 \pm 0.0068 \text{ H}_2\text{O}$  was determined gravimetrically on the basis of amount of lanthanum oxide obtained from roasting of four salt samples (~3 g each) after their previous transformation to lanthanum oxalate. Isothermal dehydration made for ~2 g salt samples consisted in their heating in weight-dryer WPE30S (RADWAG) connected *via* RS 232 joint with computer followed by registration of the changes of mass sample performed in 20 s interval with accuracy of 0.01%. For differentiation and interpolation there was used the PSI Plot program. In operation of weight-integration of third derivative it has weighted the individual interpolation loops, comparing measured masses with total mass of whole diagram and its background.

## 3. RESULTS AND DISCUSSION

Dehydration curves obtained in the process of isothermal heating of lanthanum nitrate at temperatures of 50, 60, 90 and 140 °C are presented in Figure 1.

The data presented in this figure illustrate a significant effect of temperature on dehydration rate. Differentiation of dehydration mode beginning in initial moment of heating proces was reflected in formation of two pairs of curves of similar shape. First pair was formed at temperatures of 50 and 60 °C. Dehydration curve obtained at 50 °C is indicative of rapid initial loss of two water molecules followed by formation of stable tetra-aqueous structure. A similar curve obtained for 60 °C falls sharply in the region corresponding to two water molecules and then after the loss of next water molecules stabilizes at the level corresponding to the structure containing 2.5 water molecules. The second pair of the curves shows that at 90 °C after initial sudden loss of one water molecule, further dehydration runs almost linearly and ends on tri-aqueous structure, whereas at 140 °C there forms the intermediate tri-aqueous structure, which

stabilizes after the loss of two next water molecules at the level of one-aqueous structure.

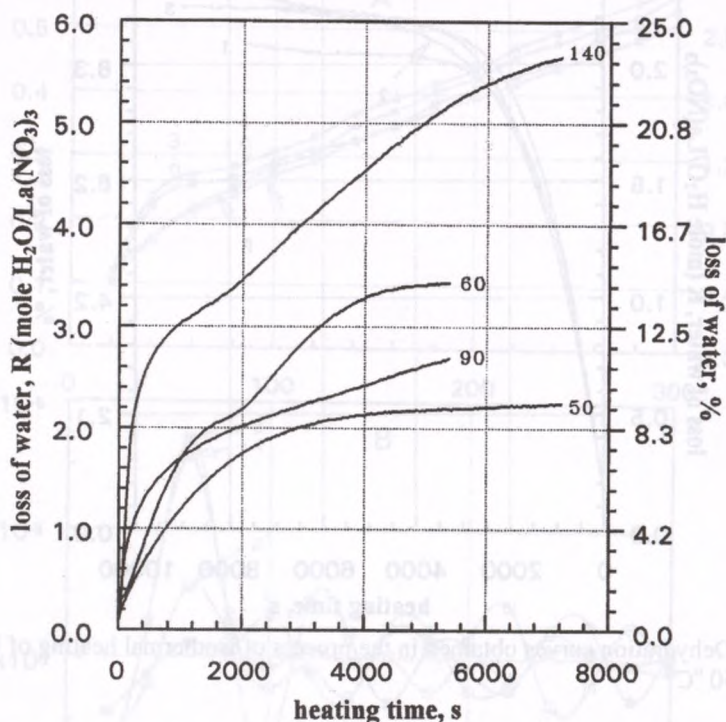


Figure 1. Dehydration curves obtained from isothermal heating of lanthanum nitrate at 50, 60, 90 and 140 °C, R - number of moles of water per 1 mol of  $\text{La}(\text{NO}_3)_3$

This differentiated mode of dehydration of lanthanum nitrate dependent on heating temperature has been fully confirmed by the results of recent investigations of Gobichon et al. [7], which using temperature-depending X-ray powder diffraction and thermogravimetric analysis for the systems, in which water-vapour pressure is greater than 4.7 Torr found the presence of five crystalline phases and one amorphous form of lanthanum nitrate.

The structures formed during low-temperature dehydration are characterized by higher stability in comparison to those formed at higher temperatures, therefore their existence at lower temperatures is more probable. Thus the recognition of conditions and mechanisms of their formation can facilitate the optimisation of separation of rare earths elements by fractional crystallization of double nitrates [8] or by solvent extraction with the use of salting agents [9].

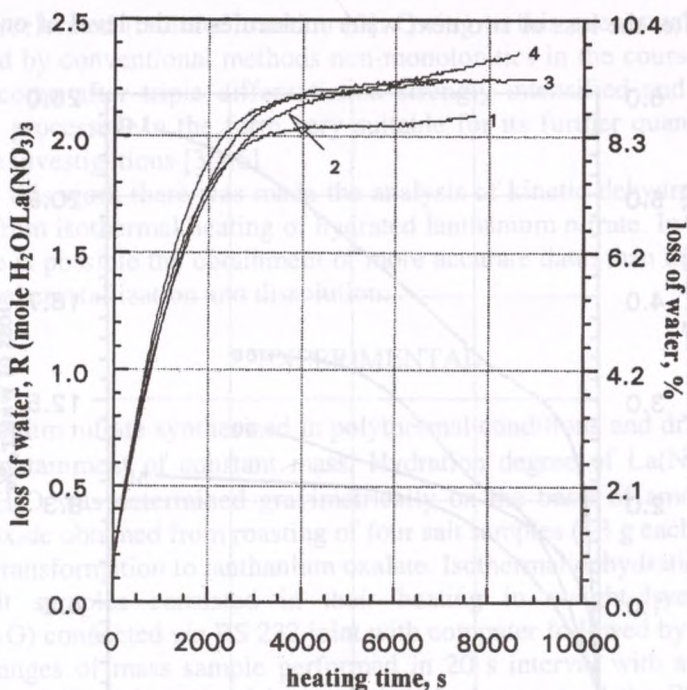


Figure 2. Dehydration curves obtained in the process of isothermal heating of lanthanum nitrate at 50 °C

Figure 2 presents the series of dehydration curves of lanthanum nitrate obtained at temperature of 50 °C. Also in this case it can distinguish two pairs of the curves characterized by similar course either on initial or on final sections. Similarly as earlier this differentiation was especially intense in initial stage of dehydration process.

For better analysis of this differentiation it has shown in Figure 3 the initial interpolation sections of individual dehydration curves (A) against a background of their third derivatives (Figure B), and in the Table 1 there are listed the values of loss of water on individual measuring points.

In first measuring point i.e. after 20 s of the heating, two pairs of the points i.e. white and black squares – from 2<sup>nd</sup> and 3<sup>rd</sup> curves have appeared at lower level, while white and black circles from 1<sup>st</sup> and 4<sup>th</sup> curves – on higher levels. In second and next measuring points there forms the next pair of the curves (3<sup>rd</sup> and 4<sup>th</sup>) illustrating the increasing rate of dehydration and second pair of the curves (1<sup>st</sup> and 2<sup>nd</sup>) corresponding to established mode of loss of water. As it can be seen from Figure 3B more rapid loss of water for third and fourth curve is seen on third derivative in the form of high maxima.

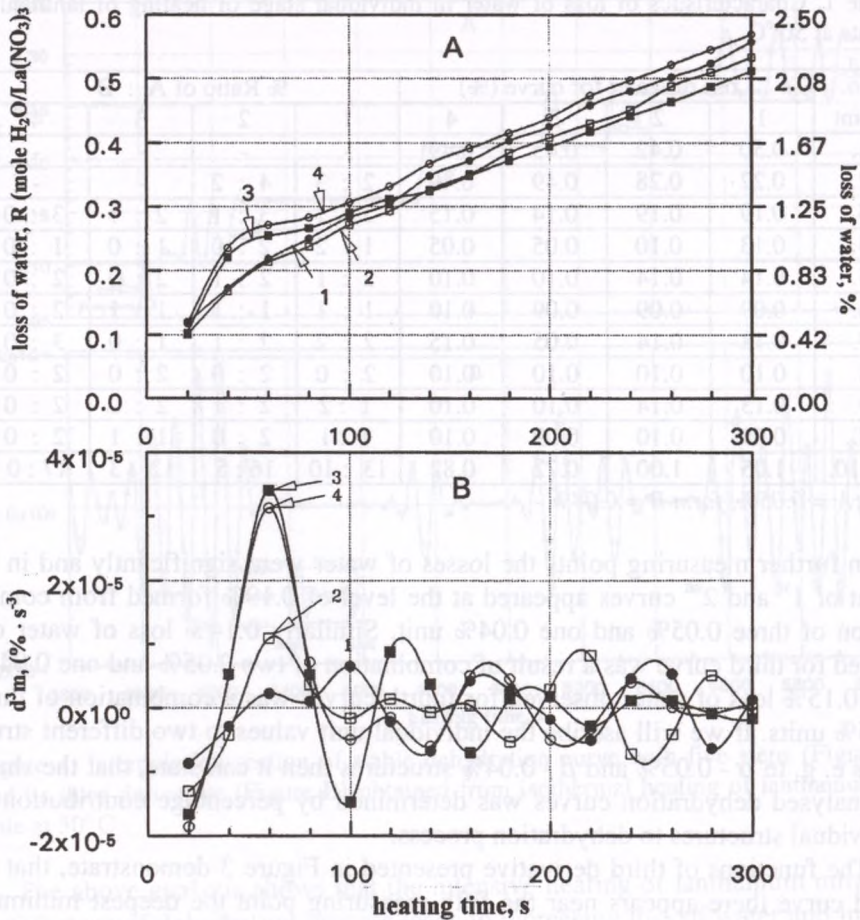


Figure 3. Initial interpolation sections of dehydration curves (Figure A) and their third derivatives (Figure B) obtained in the process of isothermal heating of lanthanum nitrate at 50 °C

The data listed in Table 1 show that water lost in unit portions 0.05 or 0.04% each or in greater portions being the multiples of unit portions. The losses of water observed after 20 s of the heating were too high in relation to unit values and in this connection the mechanism of whole process was difficult to define. However the shortening of sampling time or reduction of dehydration temperature can facilitate the analysis of initial step of dehydration process being at the same time the suitable method of examination of hydration transitions occurring e.g. in the process of polythermal crystallization [10].

Table 1. Characteristics of loss of water in individual stage of heating of lanthanum nitrate at 50 °C

No. point	Loss of water for curve (%)				% Ratio of A : B			
	1	2	3	4	1	2	3	4
1.	0.50	0.42	0.43	0.49	-	-	-	-
2.	0.22	0.28	0.49	0.49	2 : 3	4 : 2	-	-
3.	0.19	0.19	0.14	0.15	3 : 1	3 : 1	2 : 1	3 : 0
4.	0.13	0.10	0.05	0.05	1 : 2	2 : 0	1 : 0	1 : 0
5.	0.14	0.14	0.10	0.10	2 : 1	2 : 1	2 : 0	2 : 0
6.	0.09	0.09	0.09	0.10	1 : 1	1 : 1	1 : 1	2 : 0
7.	0.18	0.14	0.05	0.15	2 : 2	2 : 1	1 : 0	3 : 0
8.	0.10	0.10	0.10	0.10	2 : 0	2 : 0	2 : 0	2 : 0
9.	0.13	0.14	0.10	0.10	1 : 2	2 : 1	2 : 0	2 : 0
10.	0.09	0.10	0.09	0.10	1 : 1	2 : 0	1 : 1	2 : 0
3 - 10.	1.05	1.00	0.72	0.82	13 : 10	16 : 5	12 : 3	17 : 0

form A = 0.05%, form B = 0.04%

In further measuring points the losses of water were significantly and in 3<sup>rd</sup> point of 1<sup>st</sup> and 2<sup>nd</sup> curves appeared at the level of 0.19% formed from combination of three 0.05% and one 0.04% unit. Similarly 0.14% loss of water observed for third curve was a result of combination of two 0.05% and one 0.04%, and 0.15% loss of water observed for fourth curves was a combination of three 0.05% units. If we will ascribe the individual unit values to two different structures e. g. to  $\alpha$  - 0.05% and  $\beta$  - 0.04% structures then it can state, that the shape of analysed dehydration curves was determined by percentage contribution of individual structures to dehydration process.

The functions of third derivative presented in Figure 3 demonstrate, that on third curve there appears near the fifth measuring point the deepest minimum illustrating the sudden changes in mass of water consisting in rapid initial loss of water and then in its rapid stabilization. Similar course of third derivative but with more shallow minima is characteristic also of 2<sup>nd</sup> and 4<sup>th</sup> dehydration curves. Completely differently it appear the picture of third derivative for first dehydration curve manifesting itself in poorly shaped extrema and in formation of high maximum near the fifth measuring point. Such diversity in behaviour of first dehydration curve results from high contribution of  $\alpha$ -structure in formation of this curves, which may be confirmed by highest value of third derivative in first measuring point.

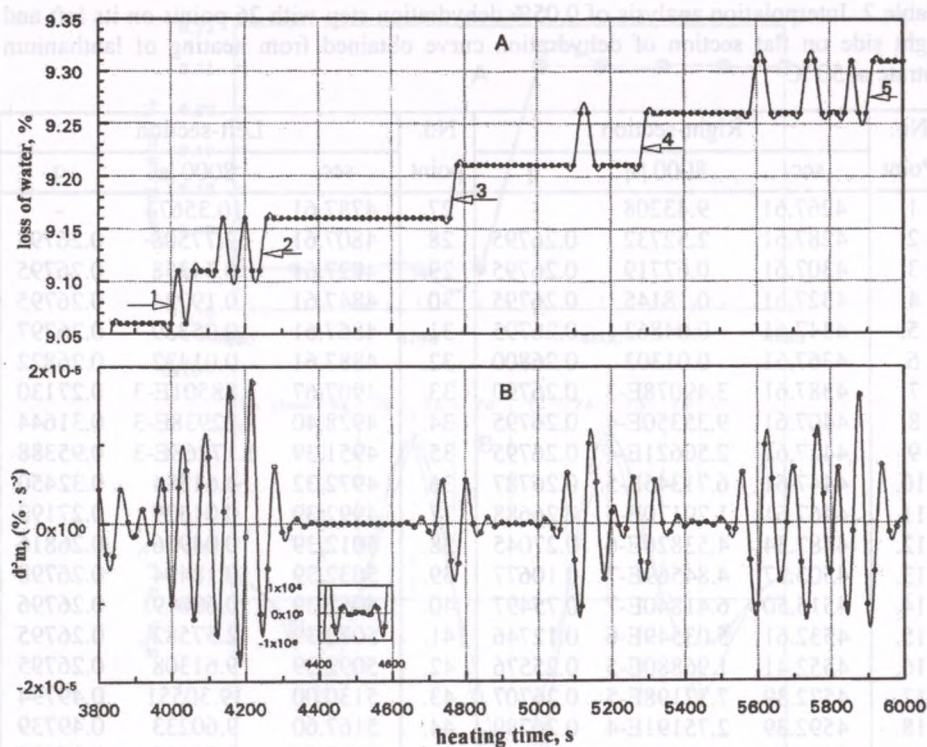


Figure 4. Interpolation section of stable dehydration curve with five steps (Figure A) and its third derivative (Figure B) obtained from isothermal heating of lanthanum nitrate at 50°C

The above analysis shows that the intensive heating of lanthanum nitrate in initial stage of dehydration process leads to increasing loss of water and in consequence to reduction of number of water molecules in first coordination sphere of lanthanum ion. Coordination sites released by water molecules were occupied by nitrate ions, which led to increase of contribution of ion-ion interactions, and new structure formed in this way became energetically more rich and less sensitive to temperature changes [11]. The mechanism of above rearrangement is confirmed by recent structural data of two polymorphic phases of lanthanum nitrate tetrahydrate determined on the basis of monochromatic X-ray powder diffraction measurements, in which  $\alpha$ -phase has a monoclinic and  $\beta$ -phase orthorhombic unit cell [12]. Friend [13] has stated also the existence of two forms of lanthanum nitrate of differentiated effect of temperature on their solubility in water.

Table 2. Interpolation analysis of 0.05% dehydration step with 26 points on its left and right side on flat section of dehydration curve obtained from heating of lanthanum nitrate at 50 °C

No. Point	Right-section			No. point	Left-section		
	sec.	8000  a	q		sec.	8000  a	q
1.	4267.61	9.43208	-	27.	4787.61	10.35674	-
2.	4287.61	2.52732	0.26795	28.	4807.61	2.77508	0.26795
3.	4307.61	0.67719	0.26795	29.	4827.61	0.74358	0.26795
4.	4327.61	0.18145	0.26795	30.	4847.61	0.19924	0.26795
5.	4347.61	0.04862	0.26795	31.	4867.61	0.05339	0.26797
6.	4367.61	0.01303	0.26800	32.	4887.61	0.01432	0.26822
7.	4387.61	3.49078E-3	0.26790	33.	4907.67	3.88501E-3	0.27130
8.	4407.61	9.35350E-4	0.26795	34.	4928.40	1.22938E-3	0.31644
9.	4427.61	2.50621E-4	0.26795	35.	4951.39	1.17268E-3	0.95388
10.	4447.61	6.71345E-5	0.26787	36.	4972.32	3.61384	0.32450
11.	4467.61	1.79170E-5	0.26688	37.	4992.39	0.01329	0.27192
12.	4487.34	4.53826E-6	0.27045	38.	5012.39	0.04956	0.26816
13.	4503.97	4.84569E-7	0.10677	39.	5032.39	0.18494	0.26798
14.	4515.50	6.41840E-7	0.75497	40.	5052.39	0.69019	0.26796
15.	4532.61	5.03549E-6	0.12746	41.	5072.39	2.57582	0.26795
16.	4552.41	1.96880E-5	0.25576	42.	5092.39	9.61308	0.26795
17.	4572.39	7.37198E-5	0.26707	43.	5130.00	19.30551	0.49794
18.	4592.39	2.75191E-4	0.26789	44.	5167.60	9.60233	0.49739
19.	4612.39	1.02705E-3	0.26794	45.	5187.54	2.53557	0.26406
20.	4632.39	3.83299E-3	0.26795	46.	5206.59	0.54857	0.21635
21.	4652.39	0.01430	0.26804	47.	5219.78	4.56947	0.12005
22.	4672.39	0.05339	0.26797	48.	5233.26	0.61088	0.13369
23.	4692.39	0.19924	0.26797	49.	5252.45	2.74155	0.22282
24.	4712.39	0.74358	0.26795	50.	5272.40	10.36129	0.26460
25.	4732.39	2.77508	0.26795	51.	5307.61	10.37769	0.99842
26.	4752.39	10.35674	0.26795		5327.61	2.77534	0.26743
				14-26	236.89	14.14746	
				26-27	35.22	96.06078	
				27-34	140.79	14.14746	
<b>Total</b>				<b>14-34</b>	<b>412.90</b>	<b>124.35580</b>	

The analysis of dehydration of lanthanum nitrate samples in successive measuring points becomes more difficult, because the contribution of individual forms in analyzed sample is variable, there is not known separately the mechanism of decomposition of each form and it is not known in which way the water evolved from one form influences the dehydration of second form. In order to establish of full mechanism of dehydration process using third derivative, there becomes necessary the analysis of single process of thermal dehydration.



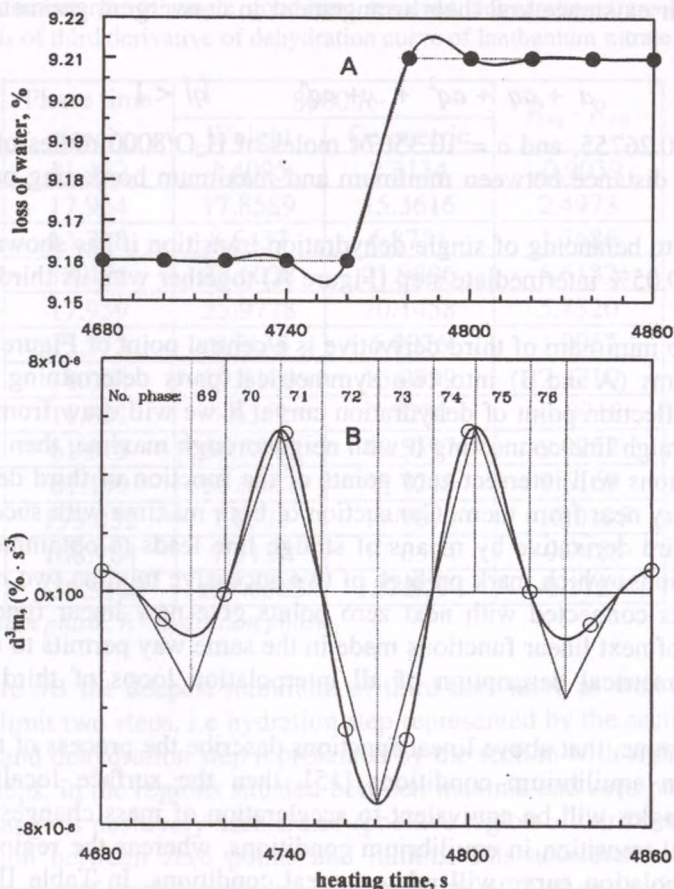


Figure 5. Quantitative analysis of good time-resolved 0.05% dehydration step (Figure A) and its third derivative (Figure B)

Figure 4A presents the interpolation section of self-stabilized third dehydration curve containing five 0.05% steps. Third step localized on most stable section of dehydration curve was 26 measuring points away the left and 26 points away the right step. As it results from Figure 5B in the region situated between second and third step the function of third derivative stabilizes strongly and transforms only seemingly to straight line, which may be testified by 2000-fold enlargement of its central section. For considered section the system is not at rest, and the cyclic nature of the changes of third derivative indicates the existence of elemental processes of dehydration and hydration similarly to in polythermal crystallization and dissolution including the elemental processes of dissolution and crystallization [3,4,6].

The periodicity of the changes occurring on horizontal sections of dehydration curve is difficult to graphical presentation, but the data listed in Table 2

confirm their existence and their arrangement in convergent geometrical series [14]:

$$a + aq + aq^2 + \dots + aq^n \quad |q| < 1 \quad (1)$$

where:  $q \approx 0.26755$ , and  $a = 10.35674$  moles of  $\text{H}_2\text{O}/8000$  moles of  $\text{La}(\text{NO}_3)_3$  denotes the distance between minimum and maximum bordening on dehydration step.

In order to balancing of single dehydration transition it has shown in Figure 5 the third 0.05% intermediate step (Figure A) together with its third derivative (Figure B).

The deep minimum of third derivative is a central point of Figure 5 dividing both diagrams (A and B) into two symmetrical parts determining simultaneously the inflection point of dehydration curve. If we will draw from this minimum the straight line connecting it with neighborhood maxima, then the formed linear functions will intersect zero points of the function of third derivative or will pass very near from them. Connection of both maxima with successive zero points of third derivative by means of straight line leads to obtainment of next linear functions, which mark on high of two successive minima two next points. These points connected with next zero points give new linear functions. The generation of next linear functions made in the same way permits to obtainment of full geometrical description of all interpolation loops of third derivative function.

If we assume, that above linear functions describe the process of thermal dehydration in equilibrium conditions [15], then the surface localized under formed triangles will be equivalent to acceleration of mass changes in considered thermal transition in equilibrium conditions, whereas the region localized under interpolation curve will relate to real conditions. In Table III there are listed some parameters of individual interpolation loops and by analogy to classical formula for the change of way in uniformly accelerated motion it has calculated the change of mass of water ( $\Delta\%$ ) in dehydration process:

$$\Delta\% = \frac{1}{2} S \cdot t^2 = \frac{1}{4} h \cdot t^3 \quad (2)$$

where:  $S$  – surface area of right triangle or interpolation loop,  $t$  – dehydration time,  $h$  – height of right triangle inscribed into interpolation loop of third derivative.

Table 3. Mass balance of single good-time resolved dehydration transition obtained from analysis of third derivative of dehydration curve of lanthanum nitrate

No. phase	Phase time (sec)	8000·R		$R_{wg} - R_{gm}$
		Weight	Geometric	
69d	11.172	1.4095	2.3134	-0.9039
70d	17.934	17.8589	15.3616	2.4973
71h	13.718	8.6437	6.8751	1.7686
72 h	18.491	28.6028	21.9896	6.6132
73d	17.959	25.9778	20.1458	5.8320
74d	13.575	8.7133	6.8076	1.9057
75h	18.064	19.0109	16.0399	2.9710
76h	11.601	1.6362	2.7280	-1.0918
69-72	61.315	56.5149	46.5397	9.9752
73-76	61.199	55.3382	45.7213	9.6169
51-68	199.032	7.8895	17.9090	-10.0195
77-86	108.964	7.9139	17.6594	-9.7455
<b>51-86</b>	<b>430.5100</b>	<b>127.6565</b>	<b>127.8294</b>	<b>-0.1729</b>

*d* - dehydration phase, *h* - hydration phase

In Figure 5B the deepest minimum of third derivative as well as the other minima delimit two steps, i.e hydration step represented by the section with left maximum and dehydration step represented by the section with right maximum. For both steps, in the regions situated between maxima and zero points the rate of mass change is positively accelerated (positive region of third derivative) and in the region between zero points and minima this acceleration is negative (negative region of third derivative). In zero points of third derivative the acceleration of hydration and dehydration rate is maximal, which corresponds to minimum and maximum localized on dehydration curve near the intermediate step.

In first highest maximum presented in Figure 5B (phase 71) there begins the dehydration process. Occurring this process vicinal and surface layers of crystalline phase are enriched in water molecules originating either from environment or from diffusion of water molecules from deeper layers. The amount of water transferred within this phase and calculated from surface area of inscribed triangle (geometrical amount) is smaller by ca. 1.7686 moles than the amount calculated from surface area of interpolation loop (weight amount). This difference appears in the form of rounded maximum and results from retarded start of hydration process. In second phase (76) the hydration process takes on more instantaneous character, which may be testified by rounded minimum and three times as large amount of water present in this phase. Also the dehydration step including 73 and 74 phases is characterized by inhibited start. However in con-

trary to hydration step, the amount of water lost in second phase of dehydration process is three times as large, than in first phase. Thus in this deep minimum containing second hydration and first dehydration, there is removed from the system almost half of total amount of water corresponding to this transitions. Residual amount of water is distributed as show Table 3 and Figure 6 symmetrically between hydration-dehydration steps localized on left and right side of analysed intermediate minimum.

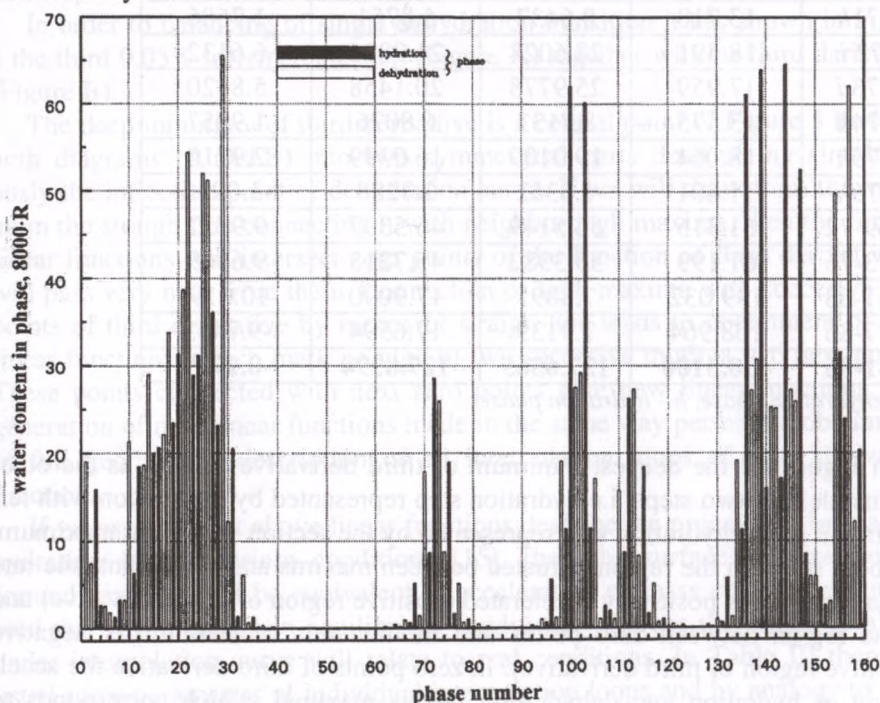


Figure 6. Molar ratio of water (8000R) in individual dehydration and hydration phases obtained from the section of dehydration curve with five 0.05% dehydration steps obtained from isothermal heating of lanthanum nitrate at 50 °C

A characteristic feature of intermediate minimum is the fact, that amount of water corresponding to hydration phase is slightly higher (by 2.6250) than this corresponding to dehydration phase. Such small advantage of hydration (72) over dehydration (73) phase was transferred from minima preceding the transition, because for nearest minimum the ratio of amounts of water corresponding to hydration and dehydration phases was 3.68 and then diminished gradually obtaining 3.14 and 2.34 for second and third, respectively. The opposite trend of the changes of inter-phase molar ratio was observed for minima formed after dehydration transition, because dehydration phase predominated over hydration one and was 3.14 and 2.27 times higher in first and second minimum, respectively.

The above analysis shows that the value of phase molar ratio within the minimum makes possible the identification and description of dehydration transition. As it results from Figure 7 the similar role may play also time phase criterion including the analysis of duration time of individual phases.

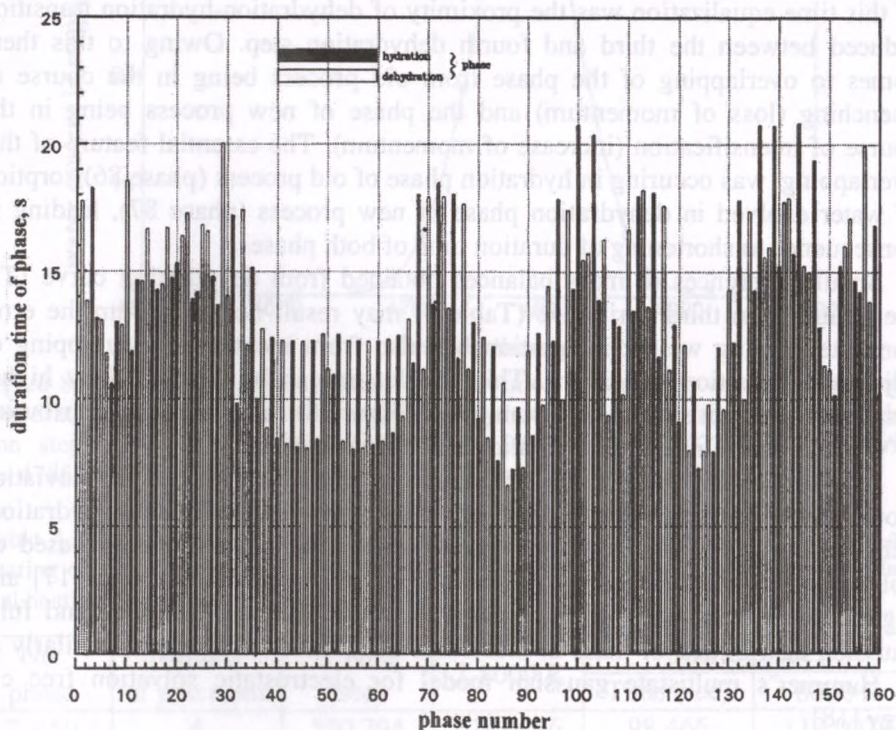


Figure 7. Duration time of individual dehydration and hydration phases on the section of dehydration curve with five 0.05% dehydration steps forming during the heating of lanthanum nitrate at 50 °C

For example, the analysis of duration time of individual phases formed in the period preceding the dehydration transition considered above indicates, that in 50<sup>th</sup> dehydration and 51<sup>th</sup> hydration phase formed positive interpolation loop of third derivative there takes place the time equalization of both phases (see magnification in Figure 4B). Significant time equalization is observed also for dehydration and hydration steps being the integral part of mentioned above interpolation loop contained 50<sup>th</sup> and 51<sup>st</sup> represents the termination of dehydration transition from second dehydration step and beginning of dehydration transition from third step. In intermediate maximum the changes of mass of water were smallest and for this reason it should assume, that the phase equalization was caused by dehydration resistance and led to prolongation of duration time of individual phases.

Another character of time phase equalization was appeared in positive interpolation loop containing 86<sup>th</sup> dehydration and 87<sup>th</sup> hydration phase and in contrary to former equalization is characterized by significantly shorter duration time and by ca. 15-fold greater amount of water. It seems that the main reason of this time equalization was the proximity of dehydration-hydration transition induced between the third and fourth dehydration step. Owing to this there comes to overlapping of the phase from old process being in the course of quenching (loss of momentum) and the phase of new process being in the course of intensification (increase of momentum). The essential feature of this overlapping was occurring in hydration phase of old process (phase 86) sorption of water evolved in dehydration phase of new process (phase 87), leading in consequence to shortening of duration time of both phases.

Small differences in mass balances obtained from dehydration curve (Table 2) and from third derivative (Table 3) may result not only from the error committed during weight integration but also from mentioned overlapping of adjoining dehydration transitions. This conclusion can be confirmed by higher dispersion on right side of Gaussian curve (Figure 8) describing the distribution of water between individual hydration and dehydration steps.

Another factors causing the differences in mass balance and the deviation from ideal gaussian distribution of mass between individual hydration-dehydration steps may be a small precision of Nspline interpolation based on polynomial of third degree [16]. The use of polynomials of fourth [17] and higher [6] degrees will permit perhaps to obtain full mass balance and fully gaussian distribution of mass in individual dehydration transitions, similarly as in Hummer's multistate gaussian model for electrostatic solvation free energy [18].

Between the third and fourth step of dehydration curve (Figure 4A) there forms the dehydration-hydration peak (Figure 4B), which is seen on the function of third derivative in the form of two positive and two negative interpolation loops of differentiated amplitudes. In deep minimum of third derivative hydration phase was more than twice greater from dehydration phase (101). Similar advantage was seen in high maximum containing hydration (103) and dehydration (102) phases.

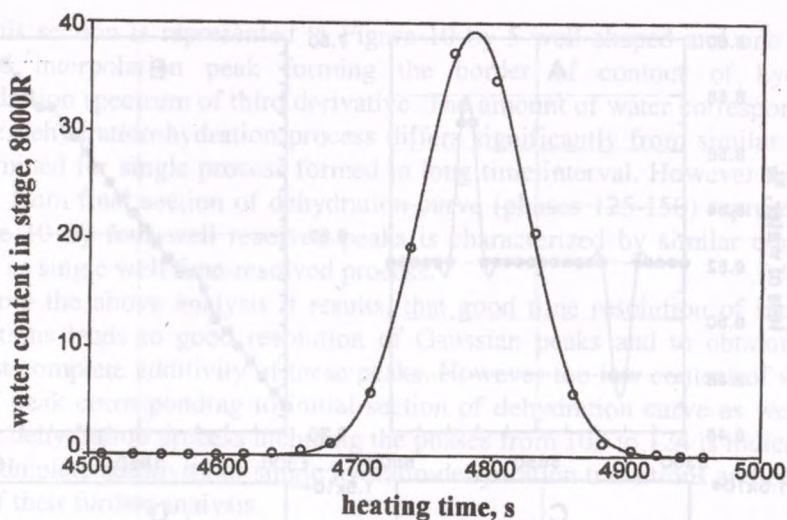


Figure 8. Gauss curve approximation of distribution of water between hydration and dehydration stages for good time-resolved dehydration transition from 0.05% dehydration step:  $y = a + b \exp(-0.5((x-c)/d)^2)$ ,  $r^2 = 0.9986$ ,  $a = 0.0226$ ,  $b = 39.1697$ ,  $c = 4785.0636$ ,  $d = 39.1697$

Table 4. Mass balance of poorly time-resolved hydration-dehydration transitions appearing on dehydration curve with five 0.05% dehydration steps obtained from isothermal heating of lanthanum nitrate at 50 °C

No. phase	Number of processes	$\Sigma$ Time (sec)	$\Sigma$ 8000·R	Single process	
				Time (sec)	8000·R
7 – 50	6	590.794	678.0176	98.466	113.0029
87 – 107	2	278.346	250.8423	139.173	125.4211
108 – 124	1	221.687	117.3201	221.687	117.3201
125 – 150	4	378.722	496.9683	94.680	124.2421

Mass balance of this transition (Table 4, phases 87-107) shows the twice higher change of mass of water in comparison to transition illustrated by single dehydration step (Table 3). This balance testifies also the equivalency of dehydration and hydration transitions.

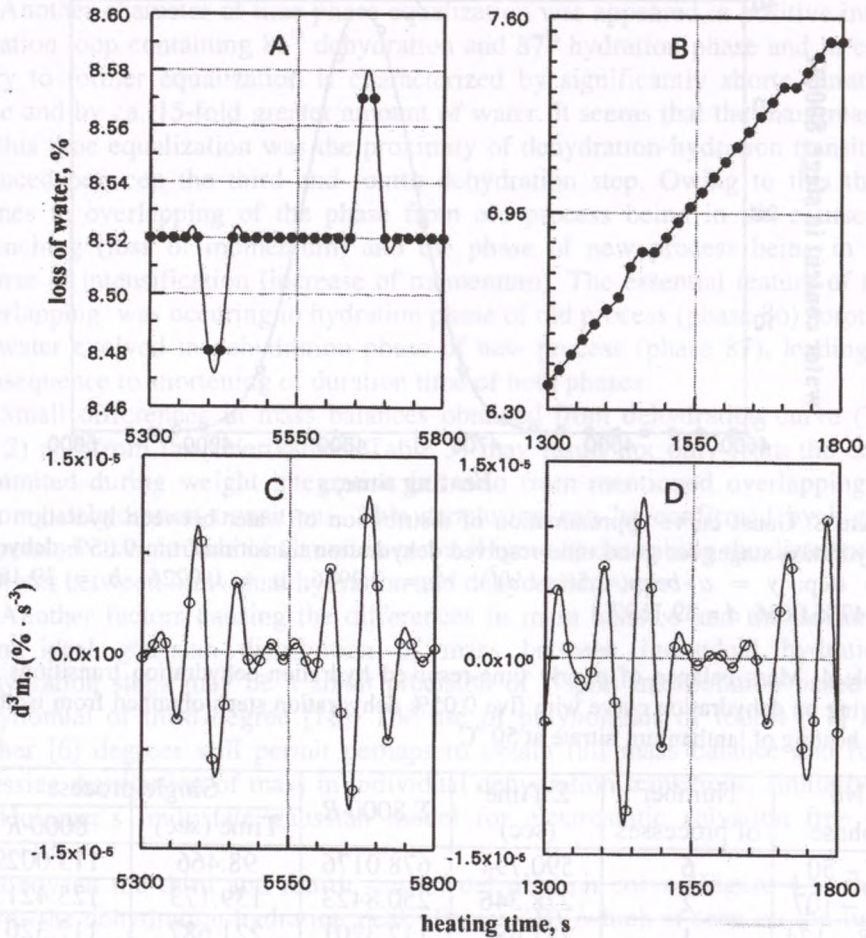


Figure 9. Characteristics of horizontal (Figure A) and ascending (Figure B) sections of dehydration curve and its third derivative (Figures C and D)

Figure 9A presents two peaks of dehydration curve with two points situated at lower i.e. 0.04% and higher i.e. 0.05% levels. Third derivative of this section of curve (Figure 9B) is almost mirror reflection of third derivative from Figure 9D obtained from differentiation of ascending part of dehydration curve presented in Figure 9C. So great similarity of the function of third derivatives indicates the possibilities of balancing of kinetic curves described by linear function.

In order to confirm such possibility there was presented in Table 4 the mass balance of initial section of dehydration curve (Figure 4, phases 5-50) containing the set of hydration-dehydration peaks with one, two or four points situated at variable 0.05% level.



This section is represented in Figure 10 by 5 well shaped and one less resolved interpolation peak forming the border of contour of hydration-dehydration spectrum of third derivative. The amount of water corresponding to single dehydration-hydration process differs significantly from similar amount determined for single process formed in long time interval. However the set of peaks from final section of dehydration curve (phases 125-150) represented in Figure 10 by four well resolved peaks is characterized by similar content of water as single well time-resolved process.

From the above analysis it results, that good time resolution of individual transitions leads to good resolution of Gaussian peaks and to obtainment of almost complete additivity of these peaks. However too low content of water in set of peak corresponding to initial section of dehydration curve as well as in single dehydration process including the phases from 108 to 124 is indicative of non-complete additivity of single hydratio-dehydration transitions and of necessity of their further analysis.

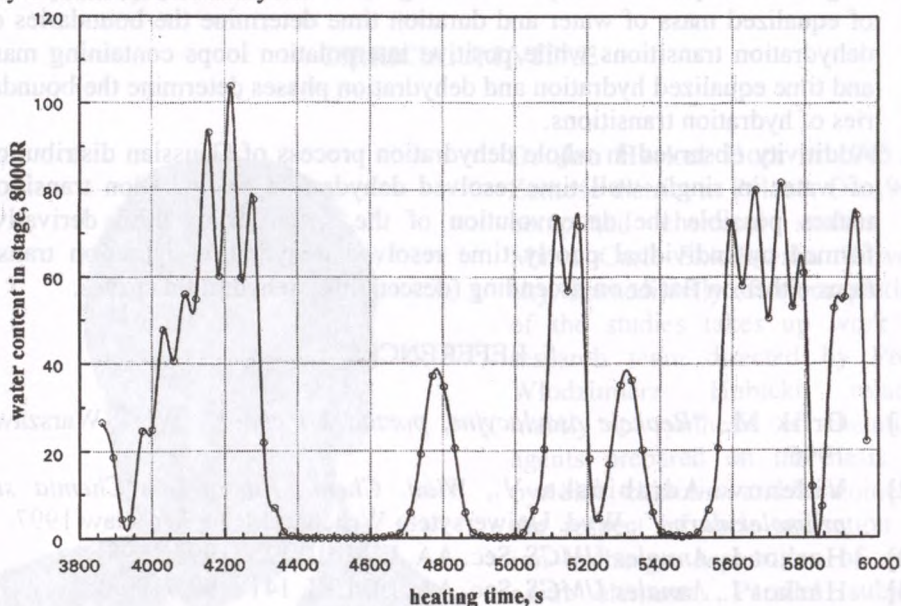


Figure 10. Interpolation of content of water in individual hydration and dehydration stages on the section of dehydration curve obtained during the heating of lanthanum nitrate at 50 °C

#### 4. CONCLUSIONS

1. The shape of dehydration curves obtained from isothermal heating of lanthanum nitrate was determined by temperature and time of heating but above all by the rate of loss of water in initial stage of dehydration process.

- Rapid initial loss of water promoted the formation of more energetically rich and more thermally stable structure of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .
2. The water was lost in unit portions 0.04 and 0.05% each or in amounts being the combination of these units and originated from different structures of lanthanum nitrate, appearing on dehydration curves in the form of single steps.
  3. Interpolation of dehydration curves and their third derivatives indicates, that unit portions of water were distributed symmetrically between dehydration and hydration phases situated on left and right sides of individual dehydration steps. Distribution of water on dehydration curve may be described by convergent geometrical series, and on third function – by gaussian curve.
  4. Surface areas of interpolation loops of third derivative and the triangles inscribed and described on these loops represent the acceleration of mass change in real and equilibrium conditions respectively.
  5. Negative interpolation loops containing hydration and dehydration phases of equalized mass of water and duration time determine the boundaries of dehydration transitions while positive interpolation loops containing mass and time equalized hydration and dehydration phases determine the boundaries of hydration transitions.
  6. Additivity observed in whole dehydration process of Gaussian distribution of water in single well time-resolved dehydration or hydration transition makes possible the deconvolution of the spectrum of third derivative formed by individual poorly time resolved dehydration-hydration transitions either on flat or on ascending (descending) dehydration curves.

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## CIRRICULUM VITAE



**Dr Jan Harkot.** Born in 1945 in Zamość district in Poland. On 1969 completed chemical studies in Maria Curie-Skłodowska University. Immediately after completion of the studies takes up work in research team directed by Prof. Włodzimierz Hubicki related mainly to synthesis of chelating agents prepared on the basis of pyridine, chinoline and benzoine in the respect of their utilisation to ion-exchange separation of rare earth elements. Parallel subject matter of his scientific interests relates to utilisation of ion-exchange for purification of water and wastes. On 1977 he obtains Ph. D. degree on the basis of dissertation entitled: "Application of ben-

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tallization. He is occupied also in recovery of rare earth elements, nickel, cobalt and manganese from industrial wastes (e. g. polishing powders, glasses, deactivated catalysts), which compose simultaneously the starting materials for preparative investigations as well as for investigations of thermochemical decomposition of water. He has elaborated and obtained a lot of technological instructions, patent pendings and proposals for an improvement.

Main area of his scientific interests includes physical chemistry of formation, dissolution and thermal decomposition of solid phases, the effect of temperature and nonaqueous solvents on acid–base equilibria and phase transitions, application of numerical methods to analysis of kinetic heating, cooling and TG curves in the respect of material engineering. Optimization of continuous and periodical counter-current crystallization methods composes important economical and ecological aspects of author's investigations related to preparation of inorganic crystalline phases.