

Determination of heats of formation of GdPO_4 and $\text{GdPO}_4 \cdot 2\text{H}_2\text{O}$ hexagonal modifications

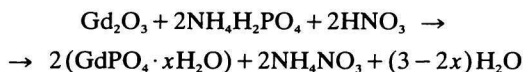
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Three samples of hexagonal modifications of hydrates of GdPO_4 were prepared, viz. $\text{GdPO}_4 \cdot 0.81\text{H}_2\text{O}$, $\text{GdPO}_4 \cdot 1.05\text{H}_2\text{O}$, and $\text{GdPO}_4 \cdot 1.41\text{H}_2\text{O}$. Heats of formation $\Delta H_{\text{m.f.}, \text{GdPO}_4, \text{hex}}$ and $\Delta H_{\text{m.f.}, \text{GdPO}_4 \cdot 2\text{H}_2\text{O}, \text{hex}}$ were calculated on the basis of Hess' law using the following data: heats of dissolution of $\text{GdPO}_4 \cdot x\text{H}_2\text{O}$, Gd_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, NH_4NO_3 , and H_2O (this paper), heat of dissolution of HNO_3 and heat of formation of reactants and products (table data). The following reaction scheme was considered



Results:

$$\frac{\Delta H_{\text{m.f.}, \text{GdPO}_4, \text{hex}}(298 \text{ K}; 0.1 \text{ MPa})}{\text{kJ mol}^{-1}} = -1924.9 \pm 15.2$$

and

$$\frac{\Delta H_{\text{m.f.}, \text{GdPO}_4 \cdot 2\text{H}_2\text{O}, \text{hex}}(298 \text{ K}; 0.1 \text{ MPa})}{\text{kJ mol}^{-1}} = -2499.3 \pm 15.4$$

The formal heat of formation of crystal water in the hexagonal modifications of hydrates of GdPO_4 is defined by the relationship

$$\Delta H_{\text{m.f.}, \text{GdPO}_4 \cdot x\text{H}_2\text{O}, \text{hex}} = \Delta H_{\text{m.f.}, \text{GdPO}_4, \text{hex}} + x\Delta H_{\text{m.f.}}$$

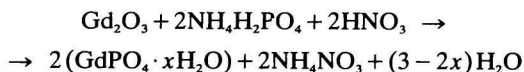
In this work the following estimated value of this quantity was used

$$\Delta H_{\text{m.f.}, \text{H}_2\text{O}, \text{cr}, \text{hex}} = -287.2 \text{ kJ mol}^{-1}$$

From the discussion of reliability of the enthalpies of formation determined in this work and those published in literature follows the recommendation for reinvestigation of the literature data on heats of formation of phosphates and

dihydrates of phosphates of Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu and dihydrates of phosphates of La, Pr, Nd, and Sm.

Были приготовлены три образца гидратов GdPO_4 гексагональной модификации: $\text{GdPO}_4 \cdot 0,81\text{H}_2\text{O}$, $\text{GdPO}_4 \cdot 1,05\text{H}_2\text{O}$ и $\text{GdPO}_4 \cdot 1,41\text{H}_2\text{O}$. Были рассчитаны теплоты образования $\Delta H_{\text{m.f.,GdPO}_4,\text{hex}}$ и $\Delta H_{\text{m.f.,GdPO}_4 \cdot 2\text{H}_2\text{O},\text{hex}}$ на основании закона Гесса с использованием следующих данных: теплот растворения $\text{GdPO}_4 \cdot x\text{H}_2\text{O}$, Gd_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, NH_4NO_3 и H_2O (в данной работе), теплоты растворения HNO_3 и теплоты образования реагентов и продуктов (табличные данные). Была рассмотрена следующая реакционная схема



Результаты:

$$\frac{\Delta H_{\text{m.f.,GdPO}_4,\text{hex}}(298 \text{ K}; 0,1 \text{ MPa})}{\text{kJ mol}^{-1}} = -1924,9 \pm 15,2$$

и

$$\frac{\Delta H_{\text{m.f.,GdPO}_4 \cdot 2\text{H}_2\text{O},\text{hex}}(298 \text{ K}; 0,1 \text{ MPa})}{\text{kJ mol}^{-1}} = -2499,3 \pm 15,4$$

Формальная теплота образования кристаллической воды в гидратах GdPO_4 гексагональной модификации определяется из соотношения

$$\Delta H_{\text{m.f.,GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}} = \Delta H_{\text{m.f.,GdPO}_4,\text{hex}} + x\Delta H_{\text{m.f.,H}_2\text{O},\text{cr,hex}}$$

В данной работе использовалось следующее оцененное значение этой величины

$$\Delta H_{\text{m.f.,H}_2\text{O},\text{cr,hex}} = -287,2 \text{ kJ mol}^{-1}$$

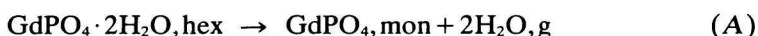
Из обсуждения достоверности энтальпий образования, найденных в данной работе и их сравнения с имеющимися в литературе данными вытекает рекомендация дополнительного пересмотра литературных теплот образования фосфатов и дигидратов фосфатов Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu и дигидратов фосфатов La, Pr, Nd и Sm.

Thermal properties of the hexagonal modification of $\text{GdPO}_4 \cdot x\text{H}_2\text{O}$ have been studied in paper [1]. The authors of the cited paper found that the reaction enthalpy of thermal dehydration of this compound (when water vapours are formed) equals $\Delta H_{\text{m,r}} = 44.7 \text{ kJ (mol (H}_2\text{O))}^{-1}$ and $47.7 \text{ kJ (mol (H}_2\text{O))}^{-1}$, which is close to the heat of evaporation of water at the temperature 298 K and pressure 0.1 MPa (this quantity equals $43.42 \text{ kJ mol}^{-1}$). (The indices have the following

meaning: m — molar, r — reaction, f — formation.) However, this result contradicts the calculated value of this quantity when the literature data [2—4] on molar enthalpy of formation of monoclinic modification of GdPO_4 ($\Delta H_{m,f,\text{GdPO}_4,\text{mon}}$ (298 K)) and the enthalpy of formation of the hexagonal modification of $\text{GdPO}_4 \cdot 2\text{H}_2\text{O}$ ($\Delta H_{m,f,\text{GdPO}_4 \cdot 2\text{H}_2\text{O},\text{hex}}$ (298 K)) are used. According to literature [2—4]

$$\frac{\Delta H_{m,r(A),(H_2O)}}{\text{kJ mol}^{-1}} = 111.2 \quad (1)$$

$\Delta H_{m,r(A),(H_2O)}$ is the reaction enthalpy related to 1 mole of H_2O according to the reaction scheme

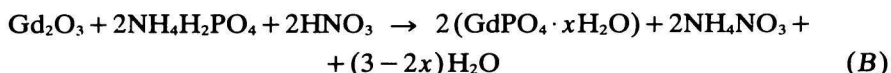


The calculated value $\Delta H_{m,r(A),(H_2O)}$ is close to the reaction heat of the thermal decomposition of some hydroxides when this quantity is related to 1 mole of H_2O . E.g. $\Delta H_{m,r}$ of decomposition of $\text{Ca}(\text{OH})_2, \text{cr} \rightarrow \text{CaO}, \text{cr} + \text{H}_2\text{O}, \text{g}$ (cr — crystal) equals $108.7 \text{ kJ mol}^{-1}$ (all conditions being the same as those used in the calculation according to eqn (1)). Since enthalpy of the change from monoclinic to more symmetric hexagonal modification is in most cases positive and relatively low the difference between the calculated value $\Delta H_{m,r(A),(H_2O)}$ according to the relationship (1) and the experimental value published in [1] can be explained by unreliability of one or both values of heats of formation of $\text{GdPO}_4, \text{mon}$ and $\text{GdPO}_4 \cdot 2\text{H}_2\text{O}, \text{hex}$ given in [2]. The aim of this work was to determine more reliable data of $\Delta H_{m,f,\text{GdPO}_4,\text{hex}}$ and $\Delta H_{m,f,\text{GdPO}_4 \cdot 2\text{H}_2\text{O},\text{hex}}$.

Experimental

Content of water in the hexagonal modifications of hydrates of phosphates of rare earths (La — Dy) is not stable [5] and it depends on the size and perfection of crystals of these substances. The better developed are the crystals, the lower is the content of water.

The following procedure was used for preparation of samples of $\text{GdPO}_4 \cdot x\text{H}_2\text{O}$. Gd_2O_3 was dissolved in mild warm diluted HNO_3 (1 volume of 65 mass % $\text{HNO}_3 + 1$ volume of H_2O). To the solution of $\text{Gd}(\text{NO}_3)_3$ heated to 40°C a five-fold surplus of $\text{NH}_4\text{H}_2\text{PO}_4$ (related to the mass of Gd_2O_3) was added. pH of the solution was adjusted to the value $\text{pH} = 7\text{—}8$ by addition of aqueous solution of NH_3 . The formation of $\text{GdPO}_4 \cdot x\text{H}_2\text{O}$ can be represented by the equation



The reaction mixture with $\text{GdPO}_4 \cdot x\text{H}_2\text{O}$ was kept at constant temperature in order to promote the growth of crystals (sample *I*: $\theta = 100^\circ\text{C}$, $t = 15$ h; sample *II*: $\theta = 70^\circ\text{C}$, $t = 16$ h; sample *III*: $\theta = 70^\circ\text{C}$, $t = 14$ h). The precipitate was filtered, washed and dried on free air. The X-ray analysis has shown that in all three cases the hexagonal modifications of hydrates of GdPO_4 were formed. Content of water in the hydrates was determined by TG analysis: sample *I* — $\text{GdPO}_4 \cdot 0.81\text{H}_2\text{O}$; sample *II* — $\text{GdPO}_4 \cdot 1.05\text{H}_2\text{O}$; sample *III* — $\text{GdPO}_4 \cdot 1.41\text{H}_2\text{O}$. $\Delta H_{\text{m},f,\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}$ was determined on the basis of the molar heats of dissolution of substances X ($\Delta H_{\text{m},\text{sol},X}(298\text{ K})$) according to the reaction scheme (B) by applying Hess' law.

The experimentally obtained values of $\Delta H_{\text{m},\text{sol},X}$ and the corresponding arithmetic means of the experimental data are summarized in Table 1. Errors of the arithmetic means were calculated using the Student coefficient for 95 % confidence limit.

Table 1

Experimental values of the heat of dissolution and their arithmetic means

Compound	$\Delta H_{\text{m},\text{sol}}/(\text{kJ mol}^{-1})$					$\Delta H_{\text{m},\text{sol},\text{ar},\text{mean}}/(\text{kJ mol}^{-1})$
Gd_2O_3	-411.2	-407.0	-413.0	-414.5		-411.4 ± 5.2
$\text{NH}_4\text{H}_2\text{PO}_4$	15.7	16.1	15.7	15.7		15.8 ± 0.3
NH_4NO_3	16.4	17.8	15.9	16.3		16.6 ± 1.3
H_2O	- 1.14	- 1.16	- 1.16	- 1.13		-1.15 ± 0.02
$\text{GdPO}_4 \cdot 0.81\text{H}_2\text{O},\text{hex}$	-44.3	-40.8	-36.2	-49.7	-35.5	-40.3 ± 2.9
$\text{GdPO}_4 \cdot 1.05\text{H}_2\text{O},\text{hex}$	-36.8	-43.3	-37.7	-39.7	-40.4	
$\text{GdPO}_4 \cdot 1.41\text{H}_2\text{O},\text{hex}$	-44.5	-34.7				

All substances were dissolved in diluted HNO_3 (1 volume of 65 mass % HNO_3 and 1 volume of H_2O) at 298 K in the calorimeter that was described elsewhere [6].

The remarkable dispersion of the obtained values of $\Delta H_{\text{m},\text{sol},\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}$ is caused by a great difference between the optimum and real deviation on the calorimetric curve.

The construction of the used calorimeter allows to obtain ΔH_{sol} with the lowest relative error of one measurement ($\delta_r = 1.4\%$) when the heat of dissolution equals ca. 130 J. If the value ΔH_{sol} is lower than an optimum value the absolute error of one measurement remains practically constant ($\delta = 1.8$ J) and therefore the corresponding relative error increases. This occurs when the substance has a low value of specific heat of dissolution as it is in the case of all three hydrates of GdPO_4 . The experimentally obtained heights of deviations on the calorimetric curves were approximately 15 times lower compared with the optimum height. As the width of the interval in which the values $\Delta H_{\text{m},\text{sol},\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}$ lie is approximate-

ly the same for all three hydrates of GdPO_4 we may consider this quantity to be the same (in limits of error of the used method) for all three substances. For calculation of $\Delta H_{m,f}$ of the anhydrous GdPO_4 and its dihydrate we used the value [2]

$$\Delta H_{m,\text{sol},\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex},\text{ar. mean}} = (-40.3 \pm 2.9) \text{ kJ mol}^{-1} \quad (2)$$

The value of $\Delta H_{m,\text{sol},\text{HNO}_3,l}$ in the used solvent was calculated (as the corresponding partial molar quantity) on the basis of the integral heat of mixing $\Delta H_{m,\text{sol}} = f(x_{\text{HNO}_3})$ obtained for the system $\text{HNO}_3\text{—H}_2\text{O}$. The value of $\Delta H_{m,\text{sol}}$ was calculated on the basis of data published in [2]. The relative error of $\Delta H_{m,\text{sol},\text{HNO}_3,l}$ is assumed to be the same as the error of determination of $\Delta H_{m,\text{sol},\text{H}_2\text{O},l}$

$$\Delta H_{m,\text{sol},\text{HNO}_3,l} = (-23.0 \pm 0.4) \text{ kJ mol}^{-1} \quad (3)$$

*Calculation of $\Delta H_{m,f,\text{GdPO}_4 \cdot 2\text{H}_2\text{O},\text{hex}}$ (298 K; 0.1 MPa)
and of $\Delta H_{m,f,\text{GdPO}_4,\text{hex}}$ (298 K; 0.1 MPa)*

Applying Hess' law one can calculate $\Delta H_{m,r(B)}$ using the heats of formation $\Delta H_{m,f,x}$ ([7]) or the heats of dissolution $\Delta H_{m,\text{sol},x}$. The index (B) denotes that the quantity corresponds to the reaction scheme (B). In the former case we obtain

$$\begin{aligned} \frac{\Delta H_{m,r(B)}}{\text{kJ mol}^{-1}} &= \frac{2\Delta H_{m,f,\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}}{\text{kJ mol}^{-1}} + 2(-365.7) + \\ &+ (3-2x)(-286.0) - (-1821.7) - 2(-1447.0) - 2(-174.3) \end{aligned} \quad (4)$$

and in the latter case it follows

$$\begin{aligned} \frac{\Delta H_{m,r(B)}}{\text{kJ mol}^{-1}} &= -411.4 + 2 \times 15.8 + 2(-23.0) - \\ &- \frac{2\Delta H_{m,\text{sol},\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}}{\text{kJ mol}^{-1}} - 2(16.6) - (3-2x)(-1.2) \end{aligned} \quad (5)$$

For the quantity $\Delta H_{m,f,\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}$ in the relationship (4) it holds

$$\Delta H_{m,f,\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}} = \Delta H_{m,f,\text{GdPO}_4,\text{hex}} + x\Delta H_{m,f,\text{H}_2\text{O},\text{cr},\text{hex}} \quad (6)$$

where $\Delta H_{m,f,\text{H}_2\text{O},\text{cr},\text{hex}}$ is the formal heat of formation of crystal water in the hexagonal modifications of hydrates of GdPO_4 . Introducing further the quantity z defined as

$$z = \Delta H_{m,f,\text{H}_2\text{O},\text{cr},\text{hex}} - \Delta H_{m,f,\text{H}_2\text{O},l} \quad (7)$$

we obtain from comparison of the right hand sides of rearranged eqn (4) (after introducing eqn (6) into this equation) and eqn (5)

$$\frac{\Delta H_{m,\text{sol},\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}}{\text{kJ mol}^{-1}} = -1965.2 - \frac{\Delta H_{m,\text{f},\text{GdPO}_4,\text{hex}}}{\text{kJ mol}^{-1}} - x(\{z\} + 1.2) \quad (8)$$

As the measured values of the molar heats of dissolution of all three hydrates cannot be distinguished in limits of the error of measurement, the most probable value of z equals

$$z = -1.2 \text{ kJ mol}^{-1} \quad (9)$$

Thus according to eqn (7) it holds

$$\Delta H_{m,\text{f},\text{H}_2\text{O},\text{cr},\text{hex}} = (-1.2 - 286.0) \text{ kJ mol}^{-1} = -287.2 \text{ kJ mol}^{-1} \quad (10)$$

and therefore eqn (8) can be transformed into relationship

$$\frac{\Delta H_{m,\text{sol},\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}}{\text{kJ mol}^{-1}} = -1965.2 - \frac{\Delta H_{m,\text{f},\text{GdPO}_4,\text{hex}}}{\text{kJ mol}^{-1}} \quad (11)$$

After introducing the experimentally determined value of $\Delta H_{m,\text{sol},\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}}$ from eqn (2) into eqn (11) we obtain the relationship

$$\frac{\Delta H_{m,\text{f},\text{GdPO}_4,\text{hex}}(298 \text{ K}; 0.1 \text{ MPa})}{\text{kJ mol}^{-1}} = -1924.9 \pm 15.2 \quad (12)$$

Introducing further eqns (10) and (12) into eqn (6) we finally obtain the equation

$$\frac{\Delta H_{m,\text{f},\text{GdPO}_4 \cdot 2\text{H}_2\text{O},\text{hex}}(298 \text{ K}; 0.1 \text{ MPa})}{\text{kJ mol}^{-1}} = -2499.3 \pm 15.4 \quad (13)$$

Errors in the determination of both quantities were calculated employing Gauss' law of spreading of errors. Errors of all quantities used in the calculation were taken into account. As $\Delta H_{m,\text{f},\text{H}_2\text{O},\text{cr},\text{hex}}$ cannot be higher than heat of formation of liquid H_2O at 298 K, the error of the former quantity was estimated to be 1.2 kJ mol^{-1}

*Discussion of reliability of the results obtained in this work
and the data for $\Delta H_{m,\text{f},\text{GdPO}_4,\text{mon}}$ and $\Delta H_{m,\text{f},\text{GdPO}_4 \cdot 2\text{H}_2\text{O},\text{hex}}$ reported in [2]*

1. The value of the quantity $\Delta H_{m,\text{f},\text{H}_2\text{O},\text{cr},\text{hex}}$ as it follows from eqn (10) differs remarkably from that calculated according to [2] ($-353.8 \text{ kJ mol}^{-1}$). It is close to $\Delta H_{m,\text{f},\text{H}_2\text{O},\text{l}}$ ($-286.0 \text{ kJ mol}^{-1}$), which gives evidence on the weak bond of water molecules in the structure of $\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}$. Similarly as "zeolite H_2O " also water in the hydrates of GdPO_4 is liberated at temperatures $< 100 \text{ }^\circ\text{C}$ and its

content is changeable and nonstoichiometric in dependence on the temperature of solution used at the preparation of these substances. In the course of heating water escapes usually in two steps ($\theta < 20^\circ\text{C}$; 100°C) and $\theta > 100^\circ\text{C}$).

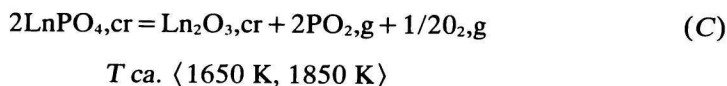
2. The value of $\Delta H_{m,f,\text{H}_2\text{O},\text{cr},\text{hex}}$ obtained from eqn (10) is also close to the value of this quantity reported for hydrates of $\text{Gd}(\text{NO}_3)_3$ [2]. It lies in the interval $(300 \text{ kJ mol}^{-1}; 307 \text{ kJ mol}^{-1})$ [2].

3. The hexagonal modifications of the hydrates of GdPO_4 which were studied in [1] were prepared by the reaction of water vapours with the products of thermal decomposition of $\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}$ which was synthesized by the procedure used in this work. Thermal behaviour of these substances, which were prepared by different experimental techniques, is practically the same.

According to [1] the compounds $\text{GdPO}_4 \cdot x\text{H}_2\text{O},\text{hex}$ have a zeolitic structure. This can explain the small difference between $\Delta H_{m,r(A)}$ $(44.7 \text{ kJ (mol(H}_2\text{O}))^{-1})$ for the first step and $47.7 \text{ kJ (mol(H}_2\text{O}))^{-1}$ for the second step of their thermal decomposition) and the heat of evaporation of water.

4. Data published in [2] are based on the results of paper [3]. The authors of the paper [3] have calculated $\Delta H_{m,f,\text{LnPO}_4 \cdot 2\text{H}_2\text{O},\text{cr}}$ on the basis of Hess' law, employing $\Delta H_{m,r}$ of precipitation of the hydrate of LnPO_4 and $\Delta H_{m,f}$ of the reactants from which the precipitate was formed. The value of $\Delta H_{m,f,\text{LnPO}_4,\text{cr}}$ was calculated on the basis of experimentally determined value of $\Delta G_{m,f,\text{LnPO}_4,\text{cr}}$ (it was obtained from the experimentally determined value of the solubility product $[\text{Ln}^{3+}][\text{PO}_4^{3-}]$) and an estimated value of $\Delta S_{m,f,\text{LnPO}_4,\text{cr}}$. Unreliability of the molar heats of formation of $\text{LnPO}_4 \cdot 2\text{H}_2\text{O}$ and LnPO_4 as published in [3] (when compared to data in [1] and in this paper) might be explained by uncorrect values of $\Delta H_{m,f}$ of reactants in the precipitation reaction, by error in determination of the product of dissolution, and/or by using a semiempirical relationship for calculation of $\Delta S_{m,f,\text{LnPO}_4,\text{cr}}$. (It should be pointed out that the editors of the tables [2] partially changed the original data published in [3].)

5. The values of $\Delta H_{m,f,\text{LnPO}_4,\text{cr}}$ used in [2] (the data were taken from paper [4]) were calculated on the basis of experimental dependence of the equilibrium values of temperature and total pressure of the gas phase of the reaction



The values $\Delta H_{m,r(C)}(T)$ were recalculated to the values $\Delta H_{m,r(C)}(T=298 \text{ K})$ using the known functions $C_x(T)$ for reactants and products (according to (C)). The value of $\Delta H_{m,f,\text{LnPO}_4,\text{cr}}$ was then obtained using Hess' law.

Unreliability of values of these quantities may originate in an inaccuracy of measurement of the total vapour pressure of gas phase in the mass spectrometer

and/or it can result from the application of unexact temperature dependences of C_x which were used in the Kirchoff equation.

Also the values of $\Delta H_{m,f,L,nPO_4,cr}$ published in [4] were modified by the editors of the thermodynamic tables [2].

As follows from this discussion the data of $\Delta H_{m,f,H_2O,cr}$ for dihydrates of orthophosphates published in the tables [2] (ca. 330 kJ mol^{-1}) are too high. As the data $\Delta H_{m,f}$ for phosphates and dihydrates of phosphates of Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu and for dihydrates of phosphates of La, Pr, Nd, Sm published in [2] were obtained using the same procedure one should also consider these data unreliable and their critical reinvestigation is needed.

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