

# Kinetics and thermodynamics of thermal decomposition of synthetic $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$

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**Abstract** The non-isothermal kinetics of dehydration of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  was studied in dynamic air atmosphere by TG–DTG–DTA at different heating rates. The result implies an important theoretical support for preparing  $\text{AlPO}_4$ . The  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  decomposes in two step reactions occurring in the range of 80–150 °C. The activation energy of the second dehydration reaction of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  as calculated by Kissinger method was found to be  $69.68 \text{ kJ mol}^{-1}$ , while the Avrami exponent value was 1.49. The results confirmed the elimination of water of crystallization, which related with the crystal growth mechanism. The thermodynamic functions ( $\Delta H^*$ ,  $\Delta G^*$  and  $\Delta S^*$ ) of the dehydration reaction are calculated by the activated complex theory. These values in the dehydration step showed that it is directly related to the introduction of heat and is non-spontaneous process.

**Keywords** Aluminium phosphate ·  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  · Non-isothermal kinetics · Thermal decomposition

## Introduction

Aluminum phosphates ( $\text{AlPO}_4$ ) are of great interest in both environmental and technological fields. In environmental field, aluminum phosphates help remove phosphate from wastewater, while their dissociations help regulate the release of phosphate in acidic soils [1]. In technological, aluminum phosphates are important in the area of catalytic reactions, such as dehydration, isomerization, polymerization, and alkylation [2]. Thus, in the last few years a series of research studies on the synthesis, characterization and catalytic activity of different  $\text{AlPO}_4$  have been undertaken [3–6]. These solids were active catalysts in several organocatalytic reactions in which textural and acid-base properties were dependent on a number of variables such as aluminum salt, precipitating agent, or calcination temperatures [2]. The key factor in obtaining  $\text{AlPO}_4$  with different properties has been the use of different preparative methods. In the literature,  $\text{AlPO}_4$  had been prepared with thermal decomposition of variscite mineral ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ),  $\text{AlPO}_4 \cdot \text{H}_2\text{O}$ -H1 and  $\text{AlPO}_4$ -21 precursors [7–9]. Thus, thermal treatment of aluminum phosphate hydrates has a great synthetic potential as they may turn simple compounds into advanced materials. The mechanism and kinetics studies of solid-state reactions are needed in order to take advantage of these potentials, which are beneficial effects on the manufacturing cost. So far, Arjona and Franco [7] studied the isothermal thermal decomposition of synthetic  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  in air using Freeman and Carroll method and reported the activation energy as  $32.6 \text{ kJ mol}^{-1}$ . However, no data on the non-isothermal kinetics, thermodynamics and mechanism of dehydration of the synthetic  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  were found in the available literature.

The present study is the first ever report entailing the reaction mechanism of thermal dehydration and application

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of the theories, viz. Kissinger [10] method for the second decomposition step of the synthetic  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ . Additionally, this study presented the kinetic parameters of the dehydration of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and suggested a correlation between the phase transition temperature peak in DTA and the assigned wavenumbers from the FTIR spectrum [11–14].

## Experimental

$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  crystalline powder was synthesized by wet chemistry method [2]. In typical procedure,  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  was prepared by precipitation from aqueous solution of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  (86.4% mass/mass) at pH = 6.1 at the “precipitation end point”, with ammonium hydroxide solution. The white powder was isolated by filtration, then washed with deionized water and dried in air.

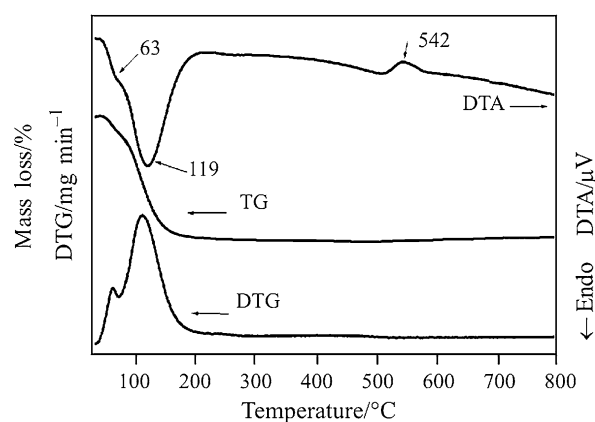
Thermal analysis measurements (thermogravimetry, TG; differential thermogravimetry, DTG; and differential thermal analysis, DTA) were carried out on a Pyris Diamond Perkin Elmer apparatus by increasing temperature from 30 to 400 °C with calcined  $\alpha\text{-Al}_2\text{O}_3$  powder as the standard reference. The experiments were carried out in air atmosphere, at heating rates of 5, 10, 15, and 20 °C  $\text{min}^{-1}$ . The sample mass was added about 6.0–10.0 mg in an aluminum crucible without pressing.

The structures of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and its final decomposition products ( $\text{AlPO}_4$ ) were studied by X-ray powder diffraction using X-ray diffractometer (Phillips PW3040, The Netherland) with  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.1546$  nm). The morphology of the selected resulting samples was examined by scanning electron microscope (SEM) using LEO SEM VP1450 after gold coating. The room temperature FTIR spectra were recorded in the range of 4000–370  $\text{cm}^{-1}$  with eight scans on a Perkin–Elmer Spectrum GX FT-IR/FT-Raman spectrometer with the resolution of 4  $\text{cm}^{-1}$  using KBr pellets (KBr, Merck, spectroscopy grade).

## Results and discussion

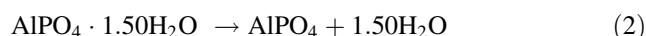
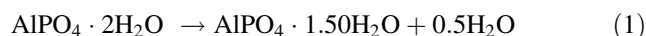
### Thermal behaviours

TG–DTG–DTA curves of the thermal decomposition of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  at the heating rate of 10 °C  $\text{min}^{-1}$  are shown in Fig. 1. The TG curve shows the two decomposition steps at temperatures below 200 °C. The elimination of water are observed in range of 70–95 and 95–150 °C with the corresponding mass losses of 5.64 and 17.26%, which correspond to 0.50 and 1.51 mol of water, respectively. The total mass loss is 22.90% corresponding to 2.01 mol of



**Fig. 1** TG–DTG–DTA curves of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  in air at heating rates of 10 °C  $\text{min}^{-1}$

water, which is close to the theoretical value of 22.79% (2.00  $\text{H}_2\text{O}$ ) for  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ . Two endothermic effects on DTA curve are observed at 63 and 119 °C, which are consistent with the DTG peaks. An exothermic effect at 542 °C without appreciable mass loss was observed in DTA curve, which could be ascribed to a transition phase from amorphous to crystalline [15]. The retained mass of about 77.10% is compatible with the value expected for the formation of  $\text{AlPO}_4$ , which is verified by XRD and FTIR measurement. The overall reaction in this work is suggested to be



The mechanism of decomposition reaction of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  in this study is different from that reported by Arjona and Franco [7], which exhibits single decomposition step. The temperature at which theoretical mass loss is achieved, can be determined from the TG curve and considered to be the minimum temperatures needed for the calcinations process. Thus,  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  sample was calcined at 250 °C for 2 h in the furnace, which is the lower temperature as compared to those of the other hydrate precursors [7–9].

The correlation between the maximum peak temperature and vibrational frequency is highly significant. The breaking bond is assimilated with a Morse oscillator [11, 12] coupled non-linear harmonic oscillators of the thermic field. The decomposition reaction takes place in the solid state, i.e. only the vibrational levels are considered. By means of the (molecular) vibrational partition functions

$$Z_v = \frac{1}{1 - e^{-x}} \quad (3)$$

the thermodynamic functions of the activated state became [12].

$$H = k_B T^2 \frac{\partial \ln Z_v}{\partial T} \quad (4)$$

and

$$s = k_B \left[ \ln Z_v + T \frac{\partial \ln z_v}{\partial T} \right] \quad (5)$$

In Eq. 1,  $x = \Theta/T$  is dimensionless and is obtained by means of the characteristic temperature

$$\Theta = \frac{hc}{k_B \omega} \quad (6)$$

where  $c$  is the light velocity and  $\omega$  is the wave number of the discussed oscillation. If  $T$  have an enough high value,  $e^x \approx 1 + x$  and consequently  $Z_v = 1/x$  and  $\partial \ln Z_v / \partial T = 1/T \approx 0$ . with these supposition,

$$\Delta S^* = b' \Delta H^* + c' \quad (7)$$

$$k_B = k_B \left[ \ln \frac{T}{\Theta} + 1 \right] \quad (8)$$

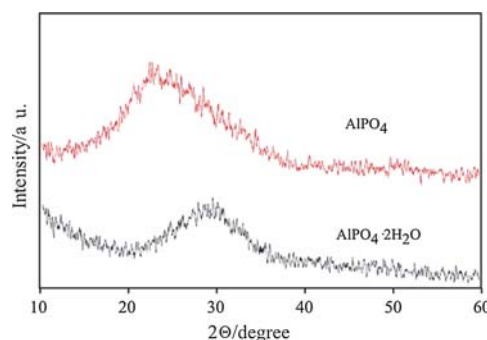
i.e.

$$T = \frac{hc}{k_B \omega} \quad (9)$$

According to Eq. 9, the phase transformation temperature peak ( $T_p$ ) in DTA or DTG can be assimilated with the characteristic temperature of the breaking bond oscillation. This equation allows a correspondence between  $T_p$  and the spectroscopic one  $\omega$ . If  $\omega$  is in  $\text{cm}^{-1}$  and  $T_p$  in K, we obtain

$$\omega_{cal} = \frac{k_B}{hc} T = 0.695T \quad (10)$$

where  $k_b$  and  $h$  are respectively the Boltzmann and Planck constants, and  $c$  the light velocity. Because the breaking of the bond has an anharmonic behavior, the specific activation is possible also due to more than one quanta, or by a higher harmonic:  $\omega_{sp} = q\omega_{calc}$ ,  $q \in N = 1, 2, 3, \dots$ , where  $\omega_{sp}$  is the assigned spectroscopic wavenumbers for the bond supposed to break. In order to corroborate the calculated data with the spectroscopic ones, we drew up the FT-IR spectra of the studied compound. According to the above-mentioned equation, the average  $T_p$  (DTA) at four heating rates (5, 10, 15, and  $20 \text{ }^\circ\text{C min}^{-1}$ ) for the two decomposition steps are 333 and 383 K. The calculated harmonic energy ( $\omega_{calc}$ ) values of the first decomposition step are 1621, 3243, and  $3475 \text{ cm}^{-1}$ , which correspond to 7, 14, and 15 quanta numbers, respectively. While the calculated harmonic energy ( $\omega_{calc}$ ) values of the second decomposition step are 1597, 3194, and  $3460 \text{ cm}^{-1}$ , which correspond to 6, 12, and 13 quanta numbers, respectively. These wavenumbers are close to the vibrational modes of water of crystallization reported in the literature [13]. The



**Fig. 2** The XRD patterns of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and its dehydration product ( $\text{AlPO}_4$ )

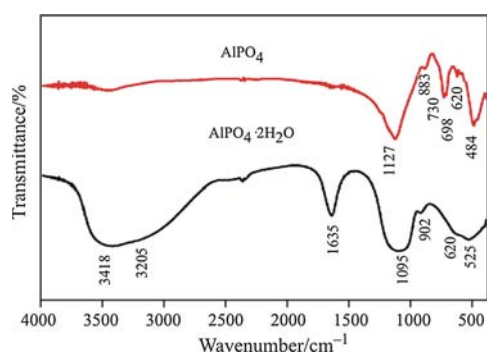
studied compound exhibited a very good agreement between the calculated wavenumbers from average  $T_p$  (DTA) and the observed wavenumbers from FT-IR spectra for the bonds suggested as being broken, which confirm two thermal decomposition steps corresponding to the loss of water of crystallization with different strength of hydrogen bonding. The calculated wavenumbers from average  $T_p$  (DTA) using Eq. 10 are convenient and simple method for the identification of the breaking bonds during the reaction, and can be used for the discussion about the decomposition steps.

#### X-ray powder diffraction

The XRD patterns of aluminum phosphate dihydrate  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and its dehydration product ( $\text{AlPO}_4$ ) are shown in Fig. 2. The problem here is that the XRD patterns show a very low degree of crystallinity. The observed broad peaks in XRD patterns indicate the predominance of the poor crystallization or amorphous phase as well as nanoparticles of these materials. This result is in good agreement with the results reported by [15], where the  $\text{AlPO}_4$  transforms from amorphous to a crystalline phase at about  $600 \text{ }^\circ\text{C}$ . It evidenced that this studied compound is a very stable inorganic framework system. Additionally, the result is consistent with a transition phase from amorphous to crystalline, which is concluded in thermal analysis.

#### Vibrational spectroscopy

FT-IR spectra of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and its dehydration product ( $\text{AlPO}_4$ ) are shown in Fig. 3. Vibrational bands are identified in relation to the crystal structure in terms of the fundamental vibrating units namely  $\text{PO}_4^{3-}$ ,  $\text{H}_2\text{O}$ , for  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{PO}_4^{3-}$  for  $\text{AlPO}_4$  [14]. FTIR spectra of  $\text{PO}_4^{3-}$  in  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{AlPO}_4$  show the antisymmetric stretching mode ( $\nu_3$ ) in  $1000\text{--}1200 \text{ cm}^{-1}$  region and the  $\nu_4$  mode in  $400\text{--}560 \text{ cm}^{-1}$  region. The observed bands in  $1600\text{--}1700 \text{ cm}^{-1}$  and  $3000\text{--}3500 \text{ cm}^{-1}$  region are



**Fig. 3** FT-IR spectra of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  and its dehydration product ( $\text{AlPO}_4$ )

attributed to the water bending and stretching vibrations. These water bands disappeared in FT-IR spectra of the calcined  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  at 250 °C. This result is in a very good agreement with the thermal analysis results and the XRD data.

### Kinetics and thermodynamic studies

The aim of the kinetic studies of TA data is to find the most probable kinetics model which gives the description of the studied decomposition process and allows the calculation of reliable values for the kinetic triplet ( $E_a$ ,  $A$  and reaction model). In the present study, the model-free and model fitting approaches were used to investigate the kinetics parameters under multiple-scan non-isothermal conditions, which are described as follow.

Dehydration of crystalline hydrates is a solid-state process of the type [16–19]:  $\text{A (solid)} \rightarrow \text{B (solid)} + \text{C (gas)}$ . The kinetics of such reactions is described by various equations taking into account the special features of their mechanisms. As one of the non-isothermal multiple-scan methods for kinetics studies, isoconversional method is also called a model-free method because no kinetic model was set before the calculation activation energy. Kissinger [10] method is a representative equation of model-free model, which is convenient to calculate the activation energy. In this kinetic study of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ , Kissinger equation was used to determine the activation energy of the dehydration step in only the second step, because the first step causes the very fast mass loss in the short temperature range (50–70 °C). Hence, the obtained data in this step will be highly sensitive to non-isothermal kinetics analysis errors [19].

The equation used for  $E_\alpha$  calculation is:

Kissinger equation:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha}\right) - \left(\frac{E_\alpha}{RT_\alpha}\right) \quad (11)$$

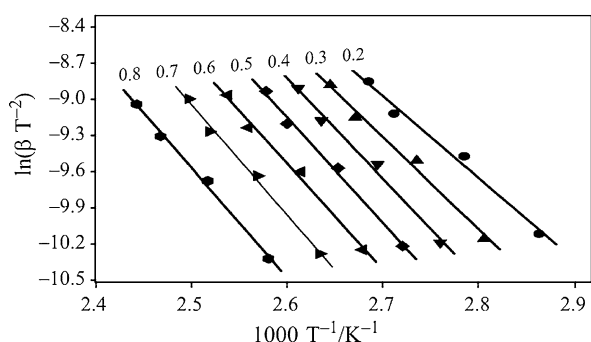
where  $A$  (the pre-exponential factor) and  $E$  (the activation energy) are the Arrhenius parameters;  $T$  is temperature (K);

$\alpha$  is the extent of conversion and  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The plot is model independent since the estimation of the apparent activation energy does not require selection of particular kinetic model (type of  $g(\alpha)$  function), which indicates that the activation energy values are usually regarded as more reliable than those obtained by a single TG curve.

According to isoconversional method, the basic data of  $\alpha$  and  $T$  collected from the TG curves of the second dehydration of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  at various heating rates (5, 10, 15 and 20 °C  $\text{min}^{-1}$ ) are illustrated in Table 1. According to the Kissinger equation, the plots of  $\ln \beta/T^2$  versus  $1000/T$  corresponding to different  $\alpha$  can be obtained by a linear regression of least-square method. The Kissinger analysis results of four TG measurements at below 200 °C are presented in Fig. 4. The activation energies  $E_\alpha$  can be calculated from the slopes of the straight lines with better linear correlation coefficient ( $r^2 > 0.99$ ), so the results are credible. The slopes change depending on  $\alpha$  for the dehydration reaction of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ . The activation energies are calculated at four different heating rates via the Kissinger method in the  $\alpha$  range of 0.2 to 0.8 as shown in Table 1. The significant change of the activation energies on  $\alpha$  (by more than 25%), lead to the conclusion that the second dehydration reaction step of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  could be multi step kinetic mechanism [16, 18]. Consequently, the estimation of the conversion function cannot be applied by any non-isothermal kinetic method such as the Coats–Redfern method. The strengths of binding between water molecules in the crystal lattice are different and, consequently, results in different dehydration temperatures and kinetic parameters. The water in crystalline hydrate may be considered either as water of crystallization (crystal water) or as co-ordinated water. The water eliminated at 150 °C and below can be considered as water of crystallization, whereas water eliminated at 200 °C and above indicates its co-ordination by the metal atom [18, 19]. Water molecules eliminated at intermediate temperatures can be co-ordinately linked water as well as co-ordinated water. The

**Table 1**  $\alpha$ – $T$  data at four heating rates ( $\beta = 5, 10, 15$  and 20 °C  $\text{min}^{-1}$ ) for the dehydration of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$

$\alpha$	Temperature at four heating rates ( $\beta/^\circ\text{C min}^{-1}$ )/K			
	$\beta = 5$	$\beta = 10$	$\beta = 15$	$\beta = 20$
0.2	349.59	359.35	368.97	372.60
0.3	356.72	365.79	374.53	378.22
0.4	362.58	371.34	379.56	383.07
0.5	367.81	377.13	384.76	388.04
0.6	373.49	382.64	390.82	394.15
0.7	379.85	389.36	397.10	400.51
0.8	387.65	397.36	405.24	409.37



**Fig. 4** Kissinger analysis of four TG measurements below 200 °C

activation energy for the elimination of water of crystallization lie in the range of 50–130  $\text{kJ mol}^{-1}$ , while the value for coordinated water are higher than this range [19]. The dehydration temperature (Fig. 1) and the calculated average activation energies (Table 2) of the second step obtained in this work suggest that the water in  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  can be considered as water of crystallization as well as crystal one. The different activation energies can be lead to the classification of the water type in crystallohydrates. Additionally, for the different materials, the loss of crystal water, ligand moieties and anionic parts does not occur in the same relative proportions. The fitting procedure also implies the mass loss steps in TG curves of various materials to be composite in nature and involving loss of various moieties in a fractional manner. The activation energies of the dehydration of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  in this study are higher than those the reported by Arjona and Franco (32.6  $\text{kJ mol}^{-1}$ ) because the different methods were applied. This indicates that the activation energy of decomposition is dependent on process and the nature of non-isothermal and isothermal methods as well as TG.

The pre-exponential factor ( $A$ ) can be estimated from the intercept of the plots of Eq. 11. All calculations were performed using a programs compiled by ourselves. The

**Table 2** Activation energies ( $E_x$ ), pre-exponential factor and correlation coefficient ( $r^2$ ) calculated by the Kissinger method for the dehydration of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$

$\alpha$	Kissinger method		
	$E_x$ ( $\text{kJ mol}^{-1}$ )	$A$ ( $\text{s}^{-1}$ )	$r^2$
0.2	56.67	$8.44 \times 10^7$	0.9934
0.3	63.75	$6.75 \times 10^8$	0.9944
0.4	69.42	$3.29 \times 10^9$	0.9950
0.5	72.72	$6.98 \times 10^9$	0.9971
0.6	73.06	$5.33 \times 10^9$	0.9957
0.7	76.10	$9.40 \times 10^9$	0.9972
0.8	76.06	$5.51 \times 10^9$	0.9979
Average	$69.68 \pm 7$	$4.47 \times 10^9$	0.9950

pre-exponential factor ( $A$ ) values in Arrhenius equation for solid phase reactions are expected to be in a wide range (six or seven orders of magnitude), even after the effect of surface area is taken into account [20, 21]. The low factors will often indicate a surface reaction, but if the reactions are not dependent on surface area, the low factor may indicate a “tight” complex. The high factors will usually indicate a “loose” complex. Even higher factors (after correction for surface area) can be obtained for complexes having free translation on the surface. Since in many cases the concentrations in solids are not controllable, it would have been convenient if the magnitude of the pre-exponential factor can provide the information for the reaction molecularity. Such a bulk decomposition, any molecule is as likely as to react with any others; and no preference is shown toward corners, edges, surface, defects or sites of previous decomposition. On the basis of these reasons, the thermal dehydration reaction of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  may be interpreted as “loose complexes”, which relates with the loss of water of crystallization. This result is in consistent with thermal analysis, which confirms that the decomposition product is aluminum phosphate ( $\text{AlPO}_4$ ).

The existence of a linear dependence between  $\ln A$  and  $E$  in a reaction described by the equation:  $\ln A = \alpha * + \beta * E$  is often discussed [16–21]. This dependence is known as kinetic compensation effect, which results from occurrences of reactions acting on active centers of different activation energies, according to the exponential distribution [12, 16, 18]. In this studied case, the apparent kinetic parameters depend on: (a) the considered range of the temperature; (b) the temperature for a given conversion degree. These results indicate that the apparent kinetic parameters are correlated with the compensation effect relationship.

The Avrami equation was also employed to describe the primary stage of non-isothermal crystallization [22–24], which is really the combined process of nucleation and growth. The most common approach used to describe the overall non-isothermal crystallization is given below:

$$n = \frac{2.5}{\Delta T} \cdot \frac{T_p^2}{E_a/R} \quad (12)$$

where  $n$  is the Avrami constant and  $\Delta T$  is the full width at half maximum of the endothermic peak;  $T_p$  is the maximum peak temperature in the endothermic peak of DTA curves and  $E_x$  is the average activation energy of the Kissinger method (Table 2).

The value of the Avrami exponent provides information regarding the morphology of the growing crystal [22–24]. The value of  $n$  reflects the mechanism dominating crystallization. Here, smaller  $n$  values indicate that the crystallization is dominated by a surface crystallization, and or



that the crystallization dimension is low. On the other hand, larger  $n$  values are expected only in case of increasing nucleation rates. For  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ , the  $n$  value is 1.49 in the dehydration step, which indicates random nucleation and growth of nuclei reaction.

From the activated complex theory (transition state) of Eyring, [25–27], the following general equation may be written:

$$A = \left( \frac{e\chi k_B T_p}{h} \right) \exp\left( \frac{\Delta S^*}{R} \right) \quad (13)$$

where  $A$  is the average activation energy  $A$  of the Kissinger method (Table 2),  $e = 2.7183$  is the Neper number;  $\chi$  transition factor, which is unity for monomolecular reactions;  $k_B$  Boltzmann constant;  $h$  Plank constant, and  $T_p$  is the peak temperature of the DTA curve. The change of the entropy may be calculated according to the formula:

$$\Delta S^* = R \ln \left( \frac{Ah}{e\chi k_B T_p} \right) \quad (14)$$

Since

$$\Delta H^* = E^* - RT_p, \quad (15)$$

when  $E^*$  is the average activation energy  $E_a$  of the Kissinger method (Table 2). The changes of the enthalpy  $\Delta H^*$  and Gibbs free energy  $\Delta G^*$  for the activated complex formation from the reagent can be calculated using the well known thermodynamic equation:

$$\Delta G^* = \Delta H^* - T_p \Delta S^* \quad (16)$$

The enthalpy of activation ( $\Delta H^*$ ), entropy of activation ( $\Delta S^*$ ), free energy of activation decomposition ( $\Delta G^*$ ) were calculated at  $T = T_p$  ( $T_p$  is the DTA peak temperature at the corresponding stage in the highest heating rate), since this temperature characterizes the highest rate of the process, which is its most important parameter.

The calculated values of  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  for the second dehydration step of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  are  $66.50 \text{ kJ mol}^{-1}$ ,  $-69.88 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $93.27 \text{ kJ mol}^{-1}$ , respectively. According to the kinetic data obtained from the TG curves, the second dehydration step has negative entropy, which indicates that the complex is not spontaneously formed. In the terms of the activated complex theory (transition theory) [25–27], a positive value of  $\Delta S^*$  indicates a malleable activated complex that leads to a large number of degrees of freedom of rotation and vibration. A result may be interpreted as a “fast” stage. On the other hand, a negative value of  $\Delta S^*$  indicates a highly ordered activated complex and the degrees of freedom of rotation as well as of vibration are less than they are in the non activated complex. The result may indicate a “slow” stage [28]. On the basis of assumptions, the second step of the thermal decomposition of

$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  may be interpreted as “slow” stage. The negative entropy also indicates a more ordered activated state that should be possible through the dehydration process. The negative value of entropy of activation is compensated by the value of the enthalpy of activation, leading to almost the same value for the free energy of activation [28]. The positive value of the enthalpy  $\Delta H^*$  is in good agreement with an endothermic effects in DTA data ( $119 \text{ }^\circ\text{C}$ ). The positive values of  $\Delta H^*$  and  $\Delta G^*$  for the dehydration stage shows that it is connected with the introduction of heat and is non-spontaneous process. These thermodynamic functions are in consistent with the results of kinetic parameters.

## Conclusions

$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  decomposes in two steps by starting after  $75 \text{ }^\circ\text{C}$  and the final product is  $\text{AlPO}_4$ . The dehydration of  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  is important for its further treatments. The final product is confirmed by XRD data and FTIR measurements. Kinetic analysis from non-isothermal TG applying model-fitting method results in a significant different values of  $E$  for different  $\alpha$  which can be assigned to multi-step reaction processes. The studied compound exhibits a very good agreement between the calculated wavenumbers from average  $T_p$  (DTA) and the observed wavenumbers from FT-IR spectra for the bonds suggested being broken, which confirms two thermal decomposition steps correspond to the loss of water of crystallization. On the basis of correctly established values of the apparent activation energy, pre-exponential factor and the changes of entropy, enthalpy and Gibbs free energy, certain conclusions can be made concerning the mechanisms and characteristics of the processes. The data of kinetics and thermodynamics play an important role in theoretical study, application development and industrial production of a title compound. In this respect, these data will be important for further studies of the title compounds. Additionally, various scientific and practical problems involving the participation of solid phases can be solved.

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