

## THE KINETICS OF THE THERMAL DEHYDRATION OF THE SYSTEM $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} - \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

TIBERIUS C. VAIMAKIS, PHILIP J. POMONIS and ANTONIOS T. SDOUKOS

*Department of Chemistry, University of Ioannina, P.O. Box 1186, Ioannina 45110 (Greece)*

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### ABSTRACT

The thermal dehydration of an equimolar mixture of the  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} - \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  system was studied using a thermobalance up to 650 °C. The weight loss takes place in two main steps, the first occurring at 90–160 °C and the second at 270–450 °C with weight losses of 13% and 8%, respectively. The dehydration was studied at heating rates of  $\beta = 2.2, 3.7, 5.8, 8.0, 9.0$  and  $10.5 \text{ }^\circ\text{C min}^{-1}$ . From the experimental results the kinetic parameters of dehydration were studied by the methods of Friedman (F), Ozawa–Flynn–Wall (OFW), Kissinger (K) and Coats–Redfern (CR) as well as by the formal kinetics (FK). The results obtained with the first two methods (F and OFW) show that both the first and the second step occur in two stages. The second stage of the first step shows an activation energy substantially less than that of the first stage. This fact might be due to diffusion limitations of water removal during the late stages of dehydration. The same fact seems to be true also for the first and second stages of the second step treated by the F and OFW methods. The other three methods (K, CR and FK) do not distinguish between the two stages noted above and the results are similar to those found for the first stage of each step. The calculated pre-exponential factors show a compensation effect of the activation energies. The results are discussed in relation to their physical meaning and in terms of the internal consistency of the methods used.

### INTRODUCTION

The mechanism of dehydration and the subsequent condensation of the  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} - \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  system have been studied previously in our laboratory [1,2] and it was found that the loss of water occurs in two main steps. The first step, which occurs between 90 and 160 °C with a weight loss of about 13%, corresponds mainly to the removal of the crystalline and zeolitic water. The second step, which occurs between 270 and 450 °C with a weight loss of 8%, yields mainly tripolyphosphate. The final products upon heating up to 650 °C were identified as  $\beta$ -metaphosphate, hexapolyphosphate and, to a lesser degree, tromelite.

The reactions describing these chemical transformations consist of a number of competitive and consecutive reaction steps [1,2] and the kinetic

analysis by thermogravimetric methods of such complex systems may lead to misleading results. However, it has been shown by Dowdy [3,4] that in the case of competitive reactions the Friedman (F) method [5] gives the true value of the instantaneous mean activation energy  $E$ , while the validity of the Ozawa [6]–Flynn–Wall [7] method (OFW) has not been proved when the reactions obey different kinetic equations. In the case of independent reactions both methods give reasonable results, but the maximum possible error of the OFW method is substantially less than that of the F method.

Elder [8] found that for independent and competitive first-order multiple reactions the correct Friedman analysis yields the same global parameters as those obtained using the Kissinger (K) method [9].

The kinetics of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  [10] and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  [11] dehydration have been studied using the formal kinetic (FK) method [12]. This method gives also the enthalpy of transformation  $\Delta H$  for which it has been recently shown [17] that the calculated values are satisfactorily accurate and can be applied even in cases of successive phenomena with uncertain limits.

Among the single thermogravimetric methods a rapid, and perhaps the most popular, one is the Coats–Redfern (CR) method [13] which gives excellent straight lines and correct  $E$  values even under extreme conditions if the correct  $n$  value of the reaction order is assumed.

In this study we continued our previous investigation [2] and report here the kinetic results of a thermogravimetric study of the  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ – $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  system made by using the methods mentioned above, namely F, OFW, CR, K and FK. Perhaps more importantly, we attempt a comparison of the results obtained with these methods.

## EXPERIMENTAL AND RESULTS

The raw materials and the method of preparation of the initial mixture had been described previously [2].

The thermogravimetric study of the equimolecular initial mixture  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ – $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  was carried out with the use of a derivatograph TRDA<sub>3</sub>-H of the Chyo Balance Corporation. The process of dehydration was performed at different heating rates ( $\beta = 2.2, 3.7, 5.8, 8.0, 9.0$  and  $10.5^\circ\text{C min}^{-1}$ ) over the temperature range  $20$ – $650^\circ\text{C}$ . The isoconversion points, from which the parameters temperature  $T$ , degree of transformation  $a$  and rate of transformation  $da/dt$  were estimated, were chosen for all the thermogravimetric curves at weight losses of 5, 7.5, 10, 12, 17.5, 18.5, 20, 21.5 and 22.5% of the sample. The total weight loss was 23.35%.

The thermal (T), thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves of the  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ – $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  equimolecular mixture at the heating rates  $\beta = 5.8$  and  $9^\circ\text{C min}^{-1}$  are shown in Fig. 1. Based on such curves, values of the

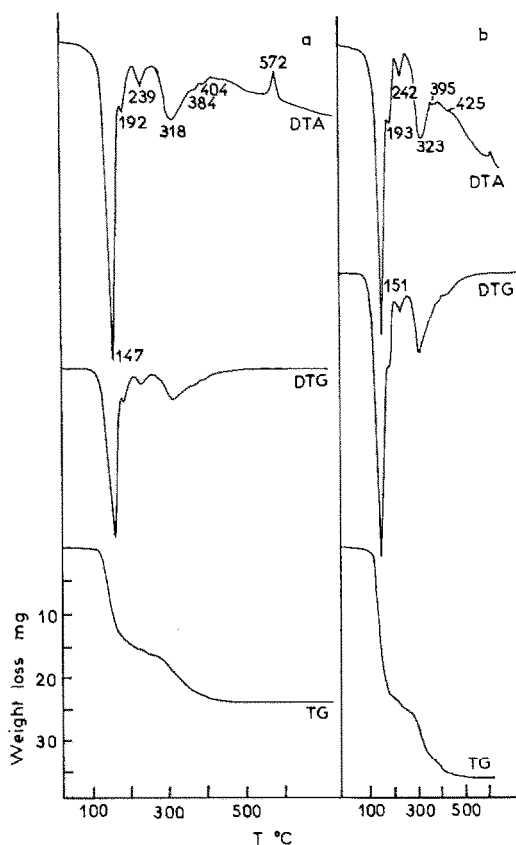


Fig. 1. TG, DTG and DTA curves of the equimolecular mixture  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} - \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . a, Heating rate  $5.8^\circ\text{C min}^{-1}$  and sample weight 100.1 mg; b, heating rate  $9.0^\circ\text{C min}^{-1}$  and sample weight 149.5 mg.

activation energy  $E$ , the pre-exponential factor  $Z$ , the order of reaction  $n$  as well as the enthalpy of the process  $\Delta H$ , when possible, were calculated as described in the following section.

## DISCUSSION

### *Theoretical principles*

Based on the above-mentioned methods the activation energy  $E$  can be calculated by several differential or integral procedures. With some of these methods the pre-exponential factor  $Z$ , the order of reaction  $n$  and the change in enthalpy  $\Delta H$  can also be found.

Friedman [5] proposed the determination of both  $E$  and  $Z$  from a number of TG curves taken at different heating rates  $\beta$ , using

$$\ln\left(\frac{da}{dt}\right)_a = \ln(ZT^m(1-a)^n) \frac{E}{RT} \quad (1)$$

When  $\ln(da/dt)$  for the same  $a$  is plotted against  $1/T$ , straight lines are obtained from which  $E$  and  $Z$  are easily calculated. The effective reaction order is calculated using [8]

$$a_m = 1 - \left[ 1 - \left( \frac{n-1}{n} \right) \eta_m \right]^{1/(n-1)} \quad (2)$$

where  $\eta_m(x) = (1 + m/x)[p_m(x)]x^{(m+2)} e^x$ ,  $\ln p_m(x) = \sum_{i=0} a_{m,i} x^i$ ,  $x = E/RT$  [16] and  $m$  is the temperature exponent of the pre-exponential term and is often taken as zero.

In the method proposed by Ozawa [6] and Flynn and Wall [7] (OFW), in which more than one thermogravimetric curve is required,  $E$  is given by eqn. (3). The major advantage of the OFW method is that it does not require any assumptions concerning the form of the kinetic equation

$$E = \frac{-R}{D} \cdot \frac{d \ln \beta}{d(1/T)} \quad (3)$$

When  $\ln \beta$ , for the same  $a$ , is plotted against  $1/T$ , straight lines are obtained. Then the slope multiplied by  $R/D$ , where  $D = 1.05$ , provides the approximate value of  $E$ , and  $D$  is re-evaluated via the empirical equation (4) and, subsequently, the correct value of  $E$  is determined.

$$D \approx 1 + \frac{1.295}{x} + \frac{0.6979}{(x + 2.475)} \quad (4)$$

In the CR method a single thermogravimetric curve is required from which the values of  $E$  and  $Z$  are calculated graphically using the equations

$$\ln \left[ \frac{-\ln(1-a)}{T^2} \right] = \ln \left[ \frac{ZR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (5)$$

for  $n = 1$  and

$$\ln \left[ \frac{1 - (1-a)^{(1-n)}}{(1-n)T^2} \right] = \ln \left[ \frac{ZR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (6)$$

for  $n \neq 1$ .

The reaction order  $n$  which yields the highest correlation coefficient of the lines  $\ln\{-\ln(1-a)/T^2\}$  or  $\ln\{[1 - (1-a)^{(1-n)}]/[(1-n)T^2]\}$  vs.  $1/T$  is accepted as representing the best reaction order.

The modified Kissinger equation [14] is employed to calculate the  $E$  and  $Z$  values from more than one DTA curve. In this method the extent of reaction ( $a_m$ ) at the temperature ( $T_m$ ) which corresponds to inflection of the DTA curve is used.

$$\ln \left( \frac{\beta}{T_m^2} \right) = \ln \left( \frac{ZR}{E} \right) + \ln \phi_m(a_m) - \frac{E}{RT_m} \quad (7)$$

where

$$\ln \phi_m(a_m) = [n - (n - 1)n] / (1 + mRT_m/E) \quad (8)$$

When  $\ln[\beta/(T_m^2)]$  is plotted vs.  $1/T$  the  $E$  and  $Z$  values are easily calculated.

The FK method [12] requires a single TG curve and its corresponding DTG curve. The parameters  $E$ ,  $Z$  and  $\Delta H$  are then calculated directly from

$$E = \frac{RT_m^2 \left( -\frac{da}{dt} \right)_m n}{\beta(1 - a_s)} \quad (9)$$

where  $a_s = 1 - a_m$ ,

$$Z = \frac{E(1 - a_s)^{(n-1)}\beta}{nRT_m^2} e^{(E/RT_m)} \quad (10)$$

and

$$\Delta H = \frac{RT_m^2 \left( -\frac{da}{dt} \right)_m}{\beta a_s} \quad (11)$$

The reaction order is calculated from [15]

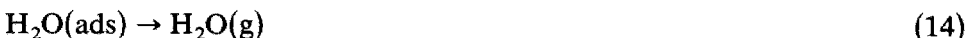
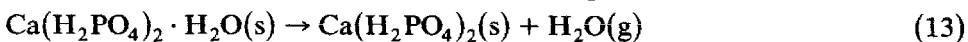
$$a_m = 1.062n^{1/(1-n)} \quad (12)$$

We now proceed to the calculation of  $E$ ,  $Z$ ,  $n$  and  $\Delta H$  parameters using the above-mentioned methods.

According to previous work [2] the thermal dehydration of the initial mixture takes place in six steps. As can be seen from Fig. 1a, for  $\beta = 5.8^\circ\text{C min}^{-1}$  these steps appear at 147, 192, 239, 318, 384 and  $404^\circ\text{C}$ . Since the intensity of the last two signals, at 384 and  $404^\circ\text{C}$ , is substantially smaller (probably less than 10%) than the peak at  $318^\circ\text{C}$  and as they are not easily separated, we decided to treat these peaks together. Conversely, the peaks at 192 and  $239^\circ\text{C}$ , which appear next to the large peak at  $147^\circ\text{C}$ , are rather small and were not therefore treated at all because of the difficulties in estimating their degrees of conversion and the corresponding temperatures.

### First step

The first step of the  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} - \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  thermal dehydration is strongly endothermic and occurs between 90 and  $160^\circ\text{C}$  with a weight loss of about 13%. This step corresponds to the removal of crystalline and zeolitic water from the initial equimolecular mixture (reactions (13) and (14)). The zeolitic water, as has been described in [2], is produced by the mechanochemical dehydration of  $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ .



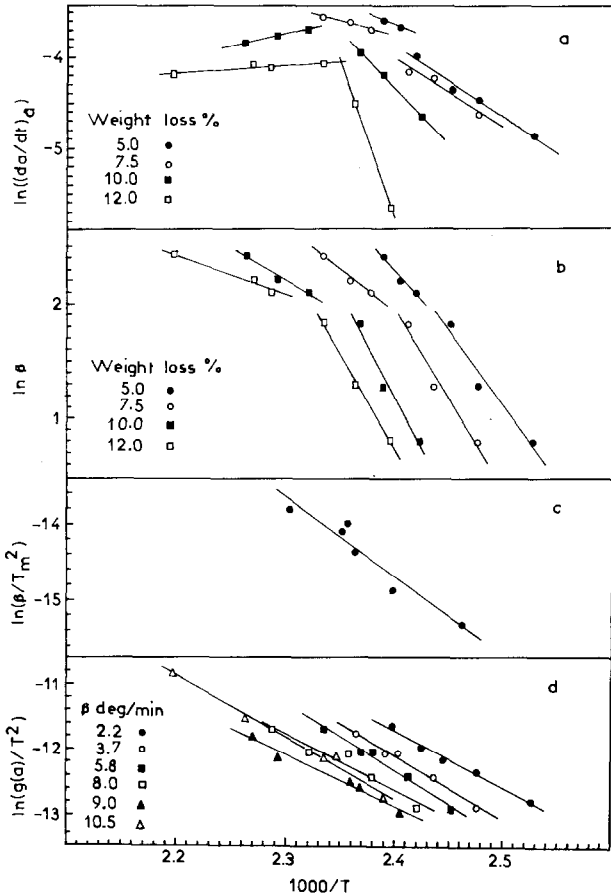


Fig. 2. Plots drawn according to the methods of (a) Friedman (eqn. (1)), (b) Ozawa-Flynn-Wall (eqn. (3)), (c) Kissinger (eqn. (7)) and (d) Coats-Redfern (eqn. (6)) for the calculation of the corresponding kinetic parameters of the first step (90–160°C) of the thermal decomposition.

Then, using the two isoconversional methods of F (Fig. 2a) and OFW (Fig. 2b) we observe that the activation energies depend on the extent of reaction and the rate of heating. Both methods show that there are two different predominant mechanisms or stages. The first stage occurs up to a heating rate of 5.8°C min<sup>-1</sup> and gives an increasing activation energy, 15.30 → 25.04 kcal mol<sup>-1</sup> by the F method and 24.80 → 31.21 kcal mol<sup>-1</sup> by the OFW method, whereas the weight loss increases from 5 to 12%. Font et al. [18] have observed that when the OFW method is applied the value of  $E$  increases at the tail of the curve, as was found in the present case. The exception to the above statement is the activation energy (69.06 kcal mol<sup>-1</sup>) calculated with the F method at 12% weight loss and at low heating rates ( $\beta = 2.2$  and 3.7°C min<sup>-1</sup>). It could be said that this fact might be due to the small number of points (just two, see Fig. 2a) from which this value was

TABLE 1

The kinetic parameters, activation energy ( $E$ , kcal mol<sup>-1</sup>), pre-exponential factor ( $Z$ , min<sup>-1</sup>), reaction order ( $n$ ) and enthalpy ( $\Delta H$ , kcal mol<sup>-1</sup>), of the first main step

Method	Weight loss (%)	$\beta$ (°C min <sup>-1</sup> )						
		2.2	3.7	5.8	8.0	9.0	10.5	
F	5	$E$	15.86				9.67	
		$Z$	$5.85 \times 10^6$				$8.72 \times 10^4$	
		$n$	0.60				0.54	
	7.5	$E$	15.30				6.19	
		$Z$	$3.23 \times 10^6$				$2.18 \times 10^3$	
		$n$	0.59				0.51	
	10	$E$	25.04				-5.07	
		$Z$	$4.44 \times 10^{11}$				$3.51 \times 10^{-3}$	
		$n$	0.62				1.14	
12	$E$	69.06(?)				-1.59		
	$Z$	$3.55 \times 10^{34}$				0.176		
	$n$	0.66				1.00		
OFW	5	$E$	24.80				19.33	
		$E$	29.91				12.88	
	7.5	$E$	34.18				9.38	
		$E$	31.21				5.21	
	12	$E$			20.39			
		$Z$			$1.04 \times 10^8$			
K	5	$n$	0.41				1.71	1.26
		$E$	19.05				15.39	19.08
		$Z$	$2.11 \times 10^9$				$2.50 \times 10^7$	$3.45 \times 10^9$
	7.5	$n$	0.50				0.67	1.50
		$E$	16.63				15.39	19.08
		$Z$	$9.44 \times 10^7$				$2.50 \times 10^7$	$3.45 \times 10^9$
CR	10	$n$	0.61				1.71	1.26
		$E$	19.05				15.39	19.08
		$Z$	$2.11 \times 10^9$				$2.50 \times 10^7$	$3.45 \times 10^9$
	12	$n$	0.50				0.67	1.50
		$E$	16.63				15.39	19.08
		$Z$	$9.44 \times 10^7$				$2.50 \times 10^7$	$3.45 \times 10^9$
FK	10	$E$	23.82				26.32	19.18
		$Z$	$2.2 \times 10^{12}$				$1.0 \times 10^{13}$	$2.6 \times 10^9$
		$n$	0.62				1.74	1.27
	12	$E$	16.60				15.28	11.79
		$Z$	$1.4 \times 10^{10}$				$1.0 \times 10^{13}$	$2.6 \times 10^9$
		$n$	0.41				1.74	1.27
$\Delta H$	$\Delta H$	14.30				15.28	11.79	
	$\Delta H$	10.31				15.28	11.79	

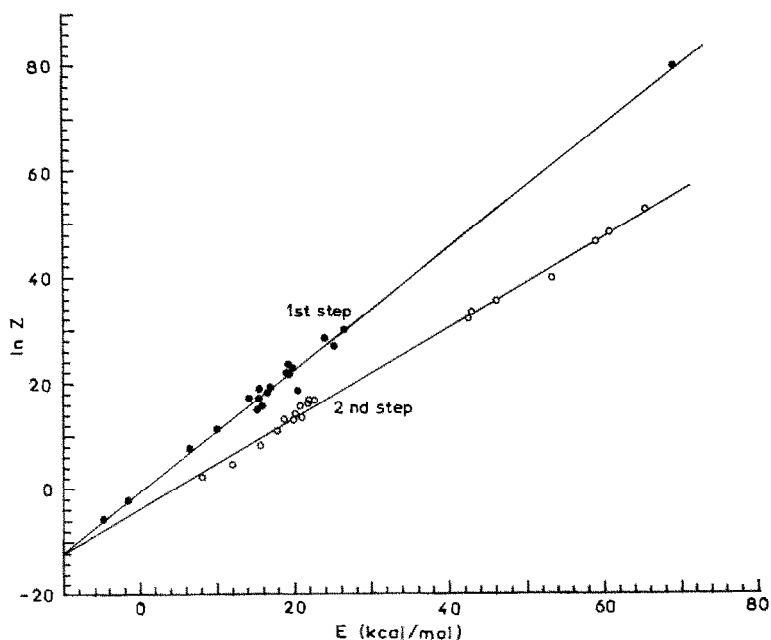


Fig. 3. Compensation effect between the parameters  $\ln Z$  and  $E$  calculated with the different methods for the two steps of decomposition.

found. However, again we observe the phenomenon that the larger the values of  $E$  in the first stage, the smaller the values of  $E$  in the second stage (see Table 1) which is not easily explained.

The reaction order of this first stage of the first step varies in a rather narrow range (0.59–0.66) while the pre-exponential factor ( $Z$ ) shows a compensation effect with  $E$  as depicted in Fig. 3.

The compensation effect between the pre-exponential factor  $Z$  and the activation energy  $E$  is a rather usual phenomenon observed in systems showing an Arrhenius-type dependence on temperature [19–23]. The explanation offered in similar cases is that they represent a parallel increment of entropic and enthalpic contribution to the rate constant [22]. However, it should also be noted that these cases may be the result of small experimental errors which are often inserted in similar calculations [21].

The second mechanism (or stage) is observed at heating rates of  $\beta = 8.0$  to  $10.5^\circ \text{C min}^{-1}$  and gives a substantially smaller activation energy as compared with the first stage (see Table 1). Perhaps more importantly,  $E$  becomes smaller with increasing weight loss, namely  $9.67 \text{ kcal mol}^{-1}$  for  $\Delta W = 5\%$  and  $6.19 \text{ kcal mol}^{-1}$  for  $\Delta W = 7.5\%$  by the F method. The negative values of  $E$  found for  $\Delta W = 10\%$  and  $12\%$  are probably meaningless. Their true value nevertheless should be nearly zero for reasons we shall discuss later. Similarly, in the OFW treatment  $E$  ( $\text{kcal mol}^{-1}$ ) drops from 19.33 to 12.88 to 9.33 to 5.21 as  $\Delta W$  (%) increases from 5 to 7.5 to 10 to 12.



We believe that this drop in activation energy of dehydration in its late stages and/or at high percentages of it, indicates that the rate-determining step is not then the chemical reaction but rather the diffusion of the water through the solid mass and away from it. It is indeed well known [24,25] that for processes where the chemical reaction and the diffusion constitute consecutive steps the apparent rate constant is given by

$$\frac{1}{k_{\text{app}}} = \frac{1}{k_{\text{true}}} + \frac{1}{D} = \frac{k_{\text{true}} + D}{k_{\text{true}} D} \quad (15)$$

where  $k_{\text{app}}$  is the apparent rate constant,  $k_{\text{true}}$  is the true rate constant and  $D$  is the diffusion coefficient. If  $D \ll k_{\text{true}}$ , then  $k_{\text{app}} \approx D$ . Since  $D$  usually does not depend on  $T$ , the result is that as the temperature increases and diffusion becomes the slow and rate-determining step the activation energy tends to zero, as was indeed observed in the present case.

The K method (Fig. 2c) gives an activation energy of 20.39 kcal mol<sup>-1</sup> and a pre-exponential factor  $Z = 1.04 \times 10^8 \text{ min}^{-1}$ . The inflection points in the DTA curves correspond to a weight loss of between 7.5 and 10% and, so the value of the activation energy agrees with the results of the first stage of the F method. The reaction orders  $n$  were calculated via eqn. (2) from all the heating rates and it was found that for  $\beta \leq 8.0^\circ \text{C min}^{-1}$  they equal about 0.5 while for  $\beta = 9.0$  and  $10.5^\circ \text{C min}^{-1}$  the orders are 1.71 and 1.26, respectively. This fact certainly indicates that a different mechanism takes over as  $\beta$  increases, as noted previously. In other words, when the sample is rapidly heated the water vapours do not have enough time to escape from the sample. The system then becomes more insensitive to temperature and in order to compensate for this an acceleration through a larger apparent reaction order occurs.

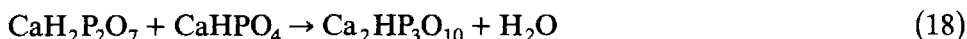
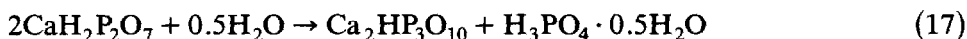
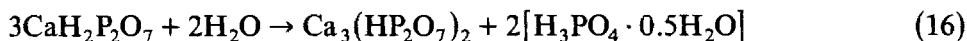
The CR method (Fig. 2d) gives a reasonable reaction order ( $n = 0.5\text{--}0.67$ ) for low heating rates;  $n$  increases to 1.5 for a heating rate of  $10.5^\circ \text{C min}^{-1}$  for reasons similar to those noted above. The activation energy is nearly constant at  $17.5 \pm 2.2 \text{ kcal mol}^{-1}$ . A compensation effect is again observed between  $E$  on the one hand and  $\ln Z$  on the other (see Fig. 3).

Finally, the FK method gives the same results as the K method. Namely, the activation energy varies in a similar range ( $20 \pm 6 \text{ kcal mol}^{-1}$ ). The reaction order for  $\beta$  up to  $8.0^\circ \text{C min}^{-1}$  is about 0.5 as previously, while for  $\beta = 9.0$  and  $10.5^\circ \text{C min}^{-1}$  the order increases to 1.74 and 1.27, respectively. The reasons for this increment have already been discussed. Note that these values are similar to those calculated with the FK method for the removal of crystalline water from  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  [10] ( $E = 19.67\text{--}21.93 \text{ kcal mol}^{-1}$ ,  $n = 0.29\text{--}0.51$  for  $\beta = 2\text{--}5^\circ \text{C min}^{-1}$  and  $n = 1.80$  for  $\beta = 10^\circ \text{C min}^{-1}$ ). The values of the enthalpy of the process vary from 10.31 to 16.60 kcal mol<sup>-1</sup> which are similar to values reported previously [10], namely 11.55–17.16 kcal mol<sup>-1</sup>. The pre-exponential factors vary from  $10^7$  to  $10^{12} \text{ min}^{-1}$ , in agreement with previously calculated values and also with those found for

pure  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  [10]. A compensation effect with  $E$  is also observed (Fig. 3).

### Second step

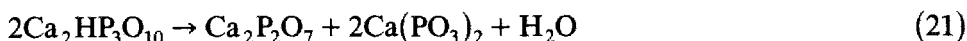
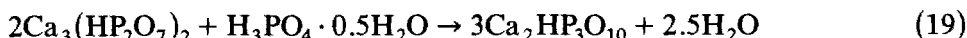
The second main step of the  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ – $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  thermal dehydration [2] is also endothermic and takes place between 270 and 450 °C with a weight loss of about 8%. According to Ref. 2 this loss corresponds to the following reactions



These reactions are not simple heterogeneous decompositions because the required water in the first two of them is produced by the last one. The third reaction (18) is a typical build-up reaction. The fact that only reaction (18) is accompanied by a weight loss while in the other two the water produced is a reactant, indicates that reaction (18) is the predominant one.

The calculation of kinetic parameters in non-isothermal conditions for such a complicated system has not been studied in detail as yet. Nevertheless, we give here the kinetic parameters calculated with various methods (see Fig. 4 and Table 2).

Note that two small steps which follow the second main step correspond to the condensation of acid salts according to the reactions (19) to (22). These small steps overlap with the main one and so their kinetic study is presented here together.



The two isoconversonal methods F (Fig. 4a) and OFW (Fig. 4b) indicate that the activation energies depend on the extent of the reaction and the rate of heating. As stated previously, both methods show two different predominant mechanisms or stages. The first mechanism is predominant up to a heating rate of  $5.8^\circ\text{C min}^{-1}$  and, according to the F method, it yields a decreasing activation energy, from 20.94 to 12.10 kcal mol<sup>-1</sup> for a 20% weight loss. The OFW method yields an increasing activation energy from 20.33 to 31.47 kcal mol<sup>-1</sup>, for a weight loss between 17.5 and 21.5% and 11.47 kcal mol<sup>-1</sup> for a 22.5% weight loss. The reaction order for this stage varies in a very narrow range from 0.72 to 0.76, while  $Z$  decreases parallel to  $E$  from  $6.34 \times 10^5$  to  $1.02 \times 10^2 \text{ min}^{-1}$ . In Fig. 3 the parallel change in  $\ln Z$

TABLE 2

The kinetic parameters, activation energy ( $E$ , kcal mol<sup>-1</sup>), pre-exponential factor ( $Z$ , min<sup>-1</sup>), reaction order ( $n$ ) and enthalpy ( $\Delta H$ , kcal mol<sup>-1</sup>), of the second main step

Method	Weight loss (%)	$\beta$ (°C min <sup>-1</sup> )					
		2.2	3.7	5.8	8.0	9.0	10.5
F	$E$		20.94				19.87
	$Z$		$6.34 \times 10^5$				$5.19 \times 10^5$
	$n$		0.76				0.74
	$E$	18.5	15.55				17.82
	$Z$		$3.79 \times 10^3$				$6.28 \times 10^4$
	$n$		0.71				0.72
OFW	$E$	20	12.10				8.07
	$Z$		$1.02 \times 10^2$				8.97
	$n$		0.72				0.71
	$E$	17.5	20.33				10.72
	$E$	18.5	23.39				10.09
	$E$	20	25.52				10.16
K	$E$	21.5	31.47				9.23
	$E$	22.5	11.47				2.82
	$E$			53.35			
	$Z$			$1.64 \times 10^{17}$			
	$n$			0.85			
	$E$		18.69				21.89
CR	$Z$		$4.32 \times 10^5$				$1.71 \times 10^7$
	$n$		1.35				2.00
	$E$	20.09	20.09				21.76
	$Z$		$1.10 \times 10^6$				$1.14 \times 10^7$
	$E$		1.50				2.00
	$n$						2.00
FK	$E$		46.08				58.99
	$Z$		$2.1 \times 10^{15}$				$1.4 \times 10^{20}$
	$n$		3.2				4.3
	$\Delta H$	32.41	24.07	21.88	22.60	29.51	30.57
	$E$		65.54				60.82
	$Z$		$5.0 \times 10^{22}$				$7.3 \times 10^{20}$

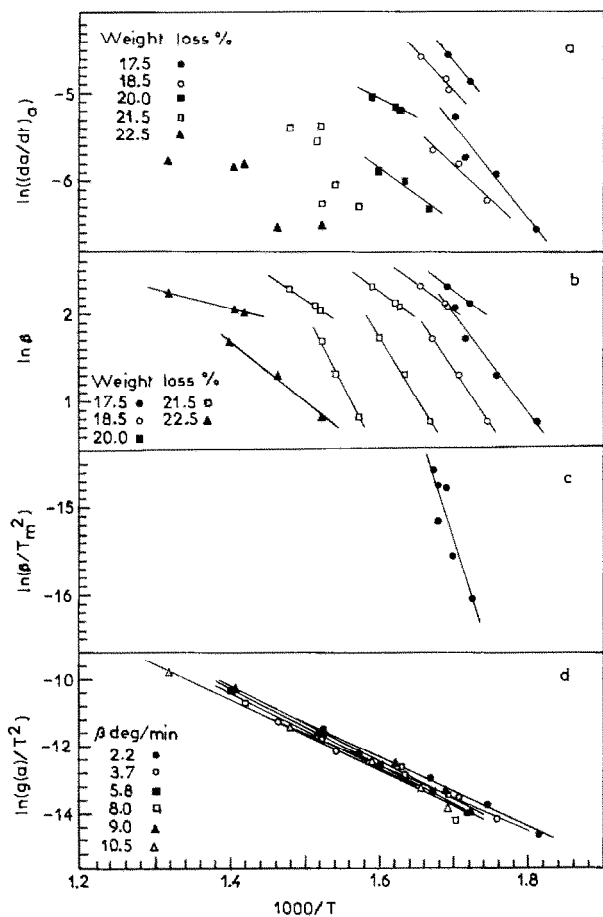


Fig. 4. As for Fig. 2 for the second step (270–450°C) of the thermal decomposition.

with  $E$  is depicted showing a behaviour similar to that found for the first step.

The second mechanism (stage) occurs at higher heating rates, namely 8.0–10.5°C min<sup>-1</sup>. The F method yields a decreasing activation energy, from 19.87 to 8.07 kcal mol<sup>-1</sup> as the weight loss increases, while by the OFW method up to 20% weight loss the activation energy is constant (10.72 kcal mol<sup>-1</sup>) and then decreases. The values of  $\ln Z$  change parallel to  $E$  as depicted in Fig. 3. As in the second stage of the first step, decreased values of activation energy should indicate that for high heating rates and/or degrees of conversion the diffusion step of water removal is mixed up with the chemical step of dehydration. According to the F method the influence of diffusion is smaller in the second than in the first step. This is equivalent to saying that if we consider the diffusion coefficient constant in both steps the chemical reaction of dehydration might be slower in the second as

compared with the first step. Indeed, the second step of dehydration as seen in Fig. 1 occurs in a rather slower pace as compared to the first one.

The K method (Fig. 4c) gives an activation energy of  $53.35 \text{ kcal mol}^{-1}$  and a pre-exponential factor of  $1.64 \times 10^{17} \text{ min}^{-1}$ . The reaction order is about 0.8.

The CR method (Fig. 4d) yields values of the reaction order larger than first order  $n = 1.35\text{--}2$ . The activation energy and pre-exponential factor are found around  $20 \text{ kcal mol}^{-1}$  and  $10^6 \text{ min}^{-1}$ , respectively. Their compensation with  $E$  is depicted in Fig. 3.

Finally, the FK method gives the highest values for activation energy, namely  $42.56\text{--}65.54 \text{ kcal mol}^{-1}$  with a mean of  $53 \text{ kcal mol}^{-1}$  and a reaction order of  $3.1\text{--}4.7$  with a mean value of 3.8. The values of the enthalpy of the process vary from  $21.88$  to  $32.41 \text{ kcal mol}^{-1}$ . The pre-exponential factors are between  $10^{13}$  and  $10^{22} \text{ min}^{-1}$ . The compensation of  $\ln Z$  with  $E$  is shown in Fig. 3.

## CONCLUSION

The thermal dehydration–condensation of the  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ – $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  system occurs in two main steps. The first step occurs between  $90$  and  $160^\circ\text{C}$  with a weight loss of 13% and the second between  $270$  and  $450^\circ\text{C}$  with a weight loss of 8%. The first step corresponds to the removal of crystalline structural water existing in the mixture. After this water removal a condensation of simple phosphates towards pyrophosphates takes place (reactions (18) to (21)) with small heat effects (Fig. 1a, peaks at  $192$  and  $239^\circ\text{C}$ ). Next, the pyrophosphates are condensed to triphosphates (reactions (15) to (17)) and this corresponds to the second step.

The kinetic parameters of the first step calculated with the F, OFW, K, CR and FK methods up to a heating rate of  $5.8^\circ\text{C min}^{-1}$  are rather similar, their values being: activation energy  $E = 20 \pm 5 \text{ kcal mol}^{-1}$ ; reaction order  $n = 0.5 \pm 0.1$ ; and  $\log Z = 8 \pm 3$ . The values of  $\ln Z$  are compensated for by  $E$  (Fig. 3).

Above the heating rate of  $5.8^\circ\text{C min}^{-1}$  a second mechanism of the thermal process is clear in the F and OFW methods. The values of  $E$  for this second stage are considerably smaller compared with the ones reported previously. Thus, the values of the activation energy found in the first stage seem to correspond to the removal of chemically adsorbed, or differently bound, water from the solids. As noted previously [2], such water molecules participate in the crystal structure of such solids, so their removal should necessitate considerable energy. For this stage all the tested methods of calculation give reasonably consistent results as long as the rate of heating is less than  $5\text{--}6^\circ\text{C min}^{-1}$ . Above this heating rate and/or for higher degrees of conversion the  $E$  values appear to decrease gradually but considerably

down to zero. This effect is due to diffusion limitations, i.e. diffusion takes over as the rate-determining step under those conditions.

The kinetic parameters of the second main step for the F, OFW, K and CR methods agree with each other to within  $25 \pm 10$  kcal mol<sup>-1</sup>. The first two methods F and OFW, that is the isoconversional ones, indicate that, somewhat similarly to the first step, two mechanisms are observed during dehydration corresponding to its early and the late stages. The FK method yields activation-energy values of around 50 kcal mol<sup>-1</sup>. The second stage of the second step appears to be related to diffusion limitation of water removal, in a manner similar to the first step. Nevertheless, since the chemical reaction in the second step seems slower than the one in the first step, diffusion does not totally control the process even at high values of  $\beta$  or  $\Delta W$ .

A useful observation is that, for the system studied, true, or nearly true, kinetic parameters, and especially activation energy values, are obtained at low heating rates  $\beta$  and small degrees of conversion  $\Delta W$ . At high  $\beta$  and  $\Delta W$  the picture is blurred by the diffusion limitation taking over the control of the system. This effect is more profound when the chemical step is fast.

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