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DEHYDRATIONS OF $Ca(H_2PO_4)_2 \cdot H_2O$ AND $Mg(H_2PO_4)_2 \cdot 2H_2O$ AND THEIR REACTIONS WITH KCl, EXAMINED WITH SIMULTANEOUS TG, DTG, DTA AND EGA

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The dehydrations of $Ca(H_2PO_4)_2 \cdot H_2O$ and $Mg(H_2PO_4)_2\ H_2O$ were examined with a simultaneous TG, DTG, DTA and EGA method, partly under conventional, and partly under quasi-isothermal and quasi-isobaric conditions. It was found among others that the dehydrations of the examined compounds took place gradually between 100 and 500°, a series of intermediates being formed. The end-products were $[Ca(PO_3)_2]_3$ and $Mg(PO_3)_2$. The reactions of these hydrates with KCl were also examined. The many subsequent part reactions could be described by the following overall equation:

$$3\ Ca(H_2PO_4)_2 + 2\ KCl = Ca_2P_2O_7 + Ca(PO_3)_2 + 2\ KPO_3 + 2\ HCl + 5\ H_2O$$

It is noteworthy that the reactions do not lead to the formation of orthophosphates, but stop after the liberation of 2 moles of HCl.

All knowledge which concerns the dehydration or other reactions of $Ca(H_2PO_4)_2 \cdot \cdot H_2O$ is important from both theoretical and practical points of view. This method has therefore been investigated by many researchers [1—21]. It was found with the help of various methods, among others thermal analysis, that the thermal decomposition of $Ca(H_2PO_4)_2 \cdot H_2O$ is a very complicated polycondensation process, in the course of which, depending on the experimental conditions, $CaH_2P_2O_7$, $Ca_3(HP_2O_7)_2$, $Ca(H_3P_2O_7)_2$ and many other forms of polyphosphates are formed as intermediates, partly in amorphous, and partly in crystalline form. The end-product of the decomposition is $[Ca(PO_3)_2]_3$, which may be amorphous or of crystalline structure.

It was recently also found [2, 6, 17, 19, 21] that in the course of the decomposition of $Ca(H_2PO_4)_2 \cdot H_2O$ "free phosphoric acid" is also formed. The curve representing the changes in the amount of phosphoric acid displays a double maximum and shows a parallel course with the DTG curve representing the rate of dehydration [19, 21]. Under given conditions about the first maximum at 280°, the presence of "free phosphoric acid" corresponding to about 15% of the P_2O_5 was detected, while in the vicinity of the second maximum at 380° the detected amount of "free phosphoric acid" corresponded to 3% of the P_2O_5 in relation to the sample amount.

The dehydration process of $Mg(H_2PO_4)_2 \cdot 2H_2O$ is less known, but it can be assumed that it has many common features with the decomposition of $Ca(H_2PO_4)_2 \cdot H_2O$.

We also examined the decompositions of $Ca(H_2PO_4)_2 \cdot H_2O$ and $Mg(H_2PO_4)_2 \cdot 2H_2O$, partly with the conventional simultaneous TG, DTG and DTA [22] method (Figs 1 and 3, curves 1, 2 and 3), partly with quasi-isothermal and quasi-isobaric thermogravimetry [23], which ensures special experimental conditions (Figs 1 and 3, curves 4). For this latter technique it is characteristic that under given conditions the transformations take place at a strictly constant rate, and in comparison to the conventional examinations are slower by one or two orders of magnitude. A further change in the experimental conditions is due to the labyrinth sample holder [23], in the inside of which the gaseous decomposition products form a "self-generated atmosphere" of 1 atm pressure. Under the mentioned experimental conditions the temperature of the sample, and the course of the TG curve traced as a function of the sample temperature change in special ways, offering further sources of information.

It could be supposed that $Ca(H_2PO_4)_2 \cdot H_2O$ and $Mg(H_2PO_4)_2 \cdot 2H_2O$ react with different salts in the solid phase, e.g. with KCl, and in the course of the reaction not only water, but also hydrochloric acid is set free. In order to study this question we applied an EGA method [24], in which the simultaneous recording of TG, DTG and DTA is also possible (Figs 2 and 4, curves 1, 2 and 3). This special method is called thermogastitrimety (TGT). The essence of this technique is as follows. The gaseous decomposition products, in the present case HCl, are con-

Table 1

Amounts of water-soluble products in heated $Ca(H_2PO_4)_2 \cdot H_2O$ and KCl mixture (weight ratio = 1 : 1) at various temperatures, given as P_2O_5 and CaO

	200°	250°	300°	350°	400°	500°		
Orthophosphate	40.9	2.6	2.5	0.8	0.2	0.1		
Pyrophosphate	1.9	13.4	6.3	2.4	1.4	0.5		
Tripolyphosphate	—	8.0	8.8	5.2	3.5	2.4		
Tetrapolyphosphate	—	4.4	5.5	4.4	3.0	1.7	%*	P_2O_5
Pentapolyphosphate	—	2.2	2.7	1.9	1.2	2.2		
Polyphosphate ($n > 5$)	—	2.9	5.6	7.5	2.2	2.8		
Trimetaphosphate	—	2.5	5.1	4.4	4.7	6.7		
Sum of phosphates	42.8	35.9	36.5	26.7	16.2	15.3	%*	P_2O_5
	76.0	63.8	64.8	47.4	28.8	27.2	%**	P_2O_5
Calcium	11.5	6.9	7.3	3.5	1.0	0.5	%*	CaO
oxide	51.7	31.0	32.8	15.7	4.5	2.2	%**	

%*: per cent relative to sample weight
%**: per cent relative to calculated amount of P_2O_5 or CaO

ducted quantitatively in an appropriate way into an absorber vessel, where they are absorbed in water, and titrated automatically with a suitable titrant, in the present case NaOH solution. With this method, the amount of hydrochloric acid (Figs 2 and 4, curves 4) and the whole course of its liberation could be established by alkalimetric titration, independently of the setting-free of water (Figs 2 and 4, curves 5).

Studies were also made of the changes in the courses of the simultaneously recorded TGT and TG curves [25] if the reaction between KCl and $Ca(H_2PO_4)_2 \cdot H_2O$ or $Mg(H_2PO_4)_2 \cdot 2H_2O$ took place under quasi-isothermal and quasi-isobaric conditions (Figs 2 and 4, curves 7 and 8).

For better evaluation of the thermoanalytical curves, an extraction method [26] was used to investigate the question of how the soluble phosphate content of the mixture changed as a function of temperature with the progress of the reaction taking place between the dehydration products of $Ca(H_2PO_4)_2 \cdot H_2O$ and KCl Table 1).

In our present paper we wish to report on the results of these examinations.

Experimental

Experiments were carried out with a Q-Derivatograph (Hungarian Optical Works, Budapest), which is suitable for simultaneous TG, DTG, DTA and TGT examinations under dynamic conditions [22, 24], as well as simultaneous TG and TGT measurements under quasi-isothermal and quasi-isobaric conditions [23, 25].

In dynamic examinations the heating rate was 10°/min, the amount of sample was about 400 mg, and the sample holder was an uncovered, conventional platinum crucible.

In quasi-isothermal – quasi-isobaric examinations the heating of the furnace was controlled so that the transformations should take place with a constant weight change of 0.5 mg/min. The amount of sample placed into the labyrinth sample holder [23] was about 400 mg.

In TGT examinations the gaseous decomposition products were transported into the absorber vessel with N_2 carrier gas streaming at 15 liter/hour. The titration was performed with 0.1 *N* NaOH solution at pH 4.5. The pH was measured with glass/calomel electrodes.

The variation in the soluble phosphate content in the course of the reaction in the mixture of $Ca(H_2PO_4)_2 \cdot H_2O + KCl$ (weight ratio = 1 : 1) was determined in the following way. With the sudden cooling-down of the sample at a given temperature, the reaction was quenched. After this the sample was powdered and then washed according to the standard method [26] for the determination of the soluble phosphate content of fertilizers. After removal of the phosphates by anion exchange, the calcium content was determined by complexometric titration [27], while the amount of condensed phosphates was measured by paper chromatography [28] and calorimetry [29]. The amount of soluble phosphates is given as P_2O_5 in Table 1, expressed partly as a percentage of $Ca(H_2PO_4) \cdot H_2O$, partly as the theoretical P_2O_5 content. The changes in the dissolved calcium content as a function of temperature are expressed in relative and absolute percentages of CaO, as can be seen in Table 1.

Chemicals

The $Ca(H_2PO_4)_2 \cdot H_2O$ examined was a p.a. preparation, powdered and washed with acetone. Chemical analysis of the sample showed that its composition was $P_2O_5 = 55.70\%$, $CaO = 22.42\%$. Accordingly, the molar ratio $CaO : P_2O_5$ was 1 : 1.02.

The $Mg(H_2PO_4)_2 \cdot 2H_2O$ sample was prepared according to [7]. After washing with acetone, it was analyzed chemically. Its composition was found to be $P_2O_5 = = 55.84\%$, $MgO = 15.85\%$. Accordingly, the molar ratio $MgO : P_2O_5$ was 1.00 : 1.00, i.e. just the theoretical.

The weight ratio in the mixtures of $Ca(H_2PO_4)_2 \cdot H_2O : KCl$ and $Mg(H_2PO_4)_2 \cdot \cdot 2H_2O : KCl$ was 1 : 1. The materials were previously finely powdered and, after weighing, thoroughly mixed for the sake of homogenization.

Discussion

$Ca(H_2PO_4)_2 \cdot H_2O$ decomposed under the conventional experimental conditions (Fig. 1, curves 1 – 3) in four stages, at about 170, 280, 320 and 430° with maximum rate (curve 2). First one mole, then again one mole, and subsequently half a mole of water departed. These two latter processes could be distinguished only on the basis of the DTG curve. Finally, again half a mole of water departed (curve 3). Of the four stages, only the first one can be interpreted. Between 120 and 200°, in all probability the crystal water was lost. Next, by polycondensation, products with ever lower water contents were formed. The composition of the sample remained strongly heterogeneous up to the end; thus the graduality of the decomposition is characteristic of the kinetics of the resultant of the part reactions rather than of their mechanism. The end-product of the decomposition at 500° was $[Ca(PO_3)_2]_3$.

The above course of the decomposition was modified somewhat if the process was examined under quasi-isothermal and quasi-isobaric conditions (Fig. 1, curve 4). It is known [2, 4, 6] that in a closed system $Ca(H_2PO_4)_2 \cdot H_2O$ melts in its own crystal water and a solution phase containing $Ca(H_2PO_4)$, $CaHPO_4$ and HPO_3 is formed, which is saturated with respect to the solid salts. After the melting in the self-generated atmosphere the solution phase gradually dried up, without any changes in the temperature. In this way about 0.5 mole of H_2O was lost. This change is indicated by the vertical part of the TG curve at 170°.

Next 1.5 moles of H_2O departed. However, the circumstance that the TG curve shows a definite break point, which corresponds to the composition $CaH_2P_2O_7$, does not mean that the composition of the sample was homogeneous at this temperature. It is far more probable that it contained not only $CaH_2P_2O_7$, but also $Ca(H_2PO_4)_2$ and various other products of different polycondensation stages,

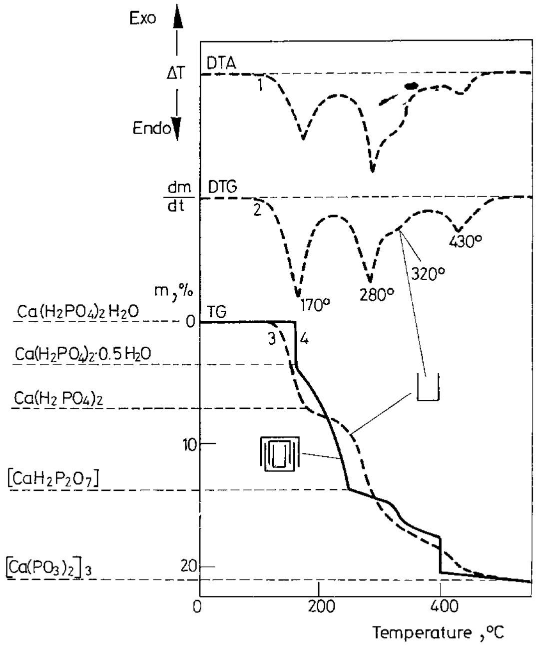

Fig. 1. Dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ under conventional (curves 1, 2, 3) and under quasi-isothermal–quasi-isobaric (curve 4) conditions

in a ratio such that the average composition of the sample was near to $CaH_2P_2O_7$.

It is noteworthy that under given conditions the last 0.5 mole of H_2O departed at 400°, at constant temperature.

Many new informations were obtained in connection with the examination of $Ca(H_2PO_4)_2 \cdot H_2O$ and KCl mixed in a weight ratio of 1 : 1. The two compounds were found to react with each other between 100 and 500° under the conventional (Fig. 2, curves 1–6) and under the quasi-isothermal-quasi-isobaric (curves 7–10) experimental conditions. Many complicated processes took place which were composed of numerous part reactions (Table 1), while H_2O and HCl were evolved. From the amounts of the reaction products, the processes could be described by the following two overall equations:

$$Ca(H_2PO_4)_2 \cdot H_2O = Ca(H_2PO_4)_2 + H_2O \tag{1}$$

$$3Ca(H_2PO_4)_2 + 2KCl = Ca_2P_2O_7 + Ca(PO_3)_2 + 2KPO_3 + 2HCl + 5H_2O. \tag{2}$$

From the magnitudes of the observed weight changes and the amount of measured HCl (Table 2), it could be concluded that, despite the fact that KCl was present in a great excess, the reaction did not continue up to the formation of orthophosphate: if we regard the conversion resulting in $CaK_4(PO_4)_2$ as end-product as the limit, then only 1/6 of the maximum theoretical amount of HCl was formed. The experiments were repeated several times and every time results were obtained which corresponded to the departure of HCl and H_2O according to Eq. (2). This could not be changed, even with a drastic alteration in the rate of the transformation under the conditions of quasi-isothermal TG and TGT examinations (Fig. 2 and Table 2).

However, we found other proof, too, that the overall reaction took place according to Eq. (2). Calculations on curves 4 and 8 of Fig. 2, which represent the course of HCl liberation, indicated a $2HCl + 5H_2O$ equivalence, and by construction curves 6 and 10 of Fig. 2 were obtained. Since these curves displayed an identical course with the TG curve, except for its initial period, it could be stated that HCl and H_2O were set free in a parallel way during the whole transformation, as had been supposed in the construction of curves 6 and 10. This, and the fact that some smaller parts of the transformation at 270 and 370° took place isothermally, may perhaps present a basis for further research into the mechanism of the reaction.

From the TG and $2HCl + 5H_2O$ curves, difference calculation permitted con-

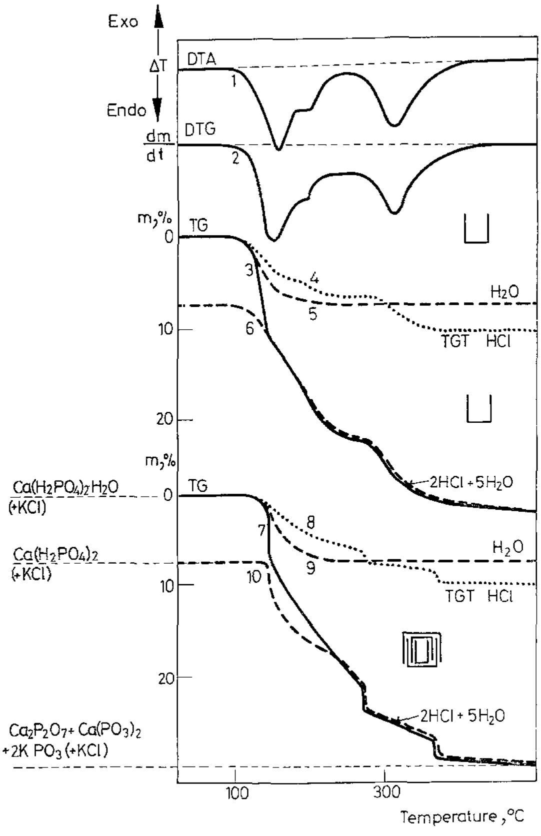

Fig. 2. Reaction between $Ca(H_2PO_4)_2 \cdot H_2O$ and KCl under conventional (curves 1—6) and under quasi-isothermal-quasi-isobaric (curves 7—10) conditions

Table 2

Calculated (Eqs 1 and 2) and measured amounts of volatile products

		Total weight	HCl	H_2O cryst.	H_2O constit.	$2\,HCl +$ $+\,5\,H_2O$
		according to curves			calculated from curves	
		TG	TGT	TG	TG + TGT	TGT
		%	%	%	%	%
$Ca(H_2PO_4)_2 \cdot H_2O$						
Theoretical values		28.6	9.6	7.1	11.9	21.5
Measured by methods	q.-isothermal	30.8	9.8	8.8	12.1	22.0
	dynamic	29.4	10.6	6.0	13.0	23.6
$Mg(H_2PO_4)_2 \cdot 2\,H_2O$						
Theoretical values		35.6	9.6	14.2	11.9	21.5
Measured by methods	q.-isothermal	35.4	10.3	12.4	12.7	23.0
	dynamic	34.7	9.6	13.3	11.8	21.4

struction of curves 5 and 9 (Fig. 2), which indicate the departure of crystal water. It thus turned out that the departure of crystal water and the course of the decomposition overlapped one another only to a small extent.

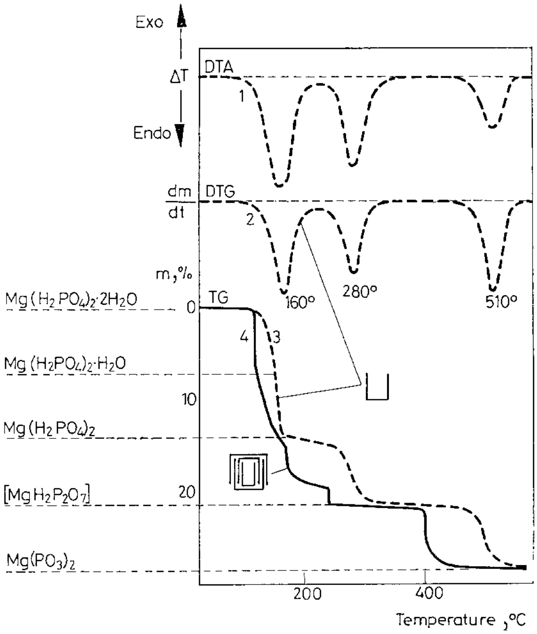

Fig. 3. Dehydration of $Mg(H_2PO_4)_2 \cdot 2\,H_2O$ under conventional (curves 1, 2, 3) and under quasi-isothermal–quasi-isobaric (curve 4) conditions

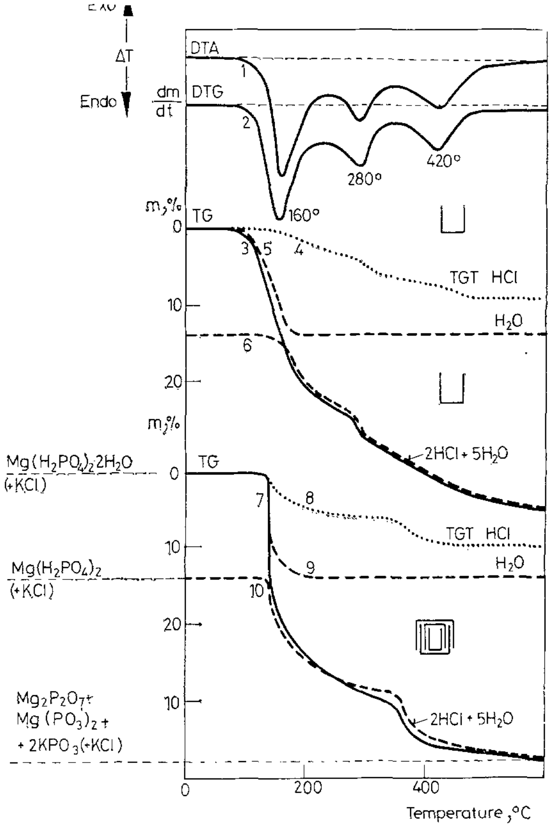

Fig. 4. Reaction between $Mg(H_2PO_4)_2 \cdot 2\ H_2O$ and KCl under conventional (curves 1—6) and under quasi-isothermal–quasi-isobaric (curves 7—10) conditions

The decomposition of $Mg(H_2PO_4)_2 \cdot 2H_2O$ differed from that of the calcium salt only slightly (Fig. 3). Under conventional experimental conditions the decomposition took place in three stages (curves 1, 2 and 3). From the aspect of the further study of the probably very complicated decomposition mechanism of the mixture, the isothermal sections at 120, 170, 240 and 400° of the TG curve traced under quasi-isothermal and quasi-isobaric conditions (curve 4) and the longer weight stability section corresponding to the composition of $MgH_2P_2O_7$ may form a basis.

The reaction mechanism for decomposition of the 1 : 1 mixture of $Mg(H_2PO_4)_2 \cdot 2H_2O$ and KCl is very similar to that of the mixture of $Ca(H_2PO_4)_2 \cdot H_2O$ and KCl, as can be judged from the curves in Fig. 4 and the data of Table 2.

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Résumé — Les auteurs ont étudié la déshydratation de $Ca(H_2PO_4)_2 \cdot H_2O$ et $Mg(H_2PO_4)_2 \cdot 2\,H_2O$. Les méthodes de TG, TGD, ATD et AGE on été utilisées simultanément en partie dans les conditions conventionelles et en partie dans les conditions quasi isothermes et quasi isobares. Les auteurs ont trouvé, entre autres, que la déshydratation de ces composés a eu lieu de façon graduelle entre 100 et 500 °C, avec formation d'une série de produits intermédiaires. Les produits finaux sont respectivement $[Ca(PO_3)_2]_3$ et $Mg(PO_3)_2$. Les auteurs ont également examiné la réaction des hydrates mentionnés avec KCl. Ils ont trouvé qu'un grand nombre de réactions partielles consécutives peut être décrit par la réaction brute suivante:

$$3\,Ca(H_2PO_4)_2 + 2\,KCl = Ca_2P_2O_7 + Ca(PO_3)_2 + 2\,KPO_3 + 2\,HCl + 5\,H_2O.$$

Il est remarquable que les réactions n'entraînent pas la formation d'orthophosphates mais qu'elles s'arrêtent après l'élimination de 2 moles de HCl.

Zusammenfassung — Die Autoren untersuchten die Dehydratisierung von $Ca(H_2PO_4)_2 \cdot H_2O$ und $Mg(H_2PO_4)_2 \cdot 2H_2O$. Zu den Untersuchungen wurde die simultane Methode von TG, DTG, DTA und EGA teils unter konventionellen, teils unter quasi isothermen und quasi isobaren Bedingungen eingesetzt. Die Autoren fanden u.a., daß die Dehydratisierung der untersuchten Verbindungen zwischen 100 und 500 °C stufenweise verlief, während eine Reihe von Zwischenprodukten gebildet wurde. Die Endprodukte waren $[Ca(PO_3)_2]_3$ bzw. $Mg(PO_3)_2$. Die Autoren prüften auch die Reaktion der erwähnten Hydrate mit KCl. Sie fanden, daß die zahlreichen aufeinanderfolgenden Teilreaktionen durch folgende Bruttoreaktion beschrieben werden können:

$$3Ca(H_2PO_4)_2 + 2KCl = Ca_2P_2O_7 + Ca(PO_3)_2 + 2KPO_3 + 2HCl + 5H_2O.$$

Es ist bemerkenswert, daß die Reaktionen nicht zur Bildung von Orthophosphaten führen, sondern daß sie nach Freisetzung zweier Moleküle von HCl zum Stillstand kommen.

Резюме — Авторы исследовали дегидратацию $Ca(H_2PO_4)_2 \cdot H_2O$ и $Mg(H_2PO_4)_2 \cdot 2H_2O$. В исследованиях одновременно был использован метод ТГ, ДТГ, ДТА и ЭГА частично при обычных и частично при квазиизотермических и квазиизобарных условиях. Авторы установили, что дегидратация исследованных соединений имела место между 100—500° и протекала последовательно и образовывался ряд промежуточных продуктов. Конечными продуктами, соответственно, были $[Ca(PO_3)_2]_3$ и $Mg(PO_3)_2$. Авторы также исследовали реакцию упомянутых гидратов с KCl. Было найдено, что многие последовательные частичные реакции могут быть описаны с помощью следующего уравнения:

$$3Ca(H_2PO_4)_2 + 2KCl = Ca_2P_2O_7 + Ca(PO_3)_2 + 2KPO_3 + 2HCl + 5H_2O$$

Замечательно, что эти реакции не приводят к образованию ортофосфатов, поскольку они останавливаются после выделения двух молекул HCl.