

STUDY OF THE SOLUBILITY DIAGRAM OF $\text{H}_3\text{PO}_4\text{-KOH-Ca(OH)}_2\text{-H}_2\text{O}$ AT 25°C Section $\text{CaHPO}_4\text{-KOH-H}_2\text{O}$

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(Received June 28, 1997; in revised form December 22, 1997)

Abstract

Study of the system $\text{CaHPO}_4\text{-KOH-H}_2\text{O}$ at 25°C allowed determination of the precipitation fields of CaHPO_4 and the apatite compounds $\text{KCaPO}_4\cdot\text{H}_2\text{O}$ and $\text{K}_4\text{Ca}(\text{PO}_4)_2\cdot 5\text{H}_2\text{O}$. The solid products were studied and identified by X-ray analysis. The water ratio is of great importance in the preparation of the starting mixture; it affects the nature of the compounds obtained after equilibrium.

Keywords: apatite, calcium phosphate, potassium phosphate, solubility diagram

Introduction

Study of the system $\text{H}_3\text{PO}_4\text{-KOH-Ca(OH)}_2\text{-H}_2\text{O}$ at 25°C began with the establishment of the section $\text{Ca}(\text{H}_2\text{PO}_4)_2\text{-KOH-H}_2\text{O}$ [1]. The present paper reports results on the system $\text{CaHPO}_4\text{-KOH-H}_2\text{O}$, which is another section of the same system.

Experimental

In consequence of the low solubility of the solid products formed in the prepared sample mixtures, the methods chosen for this work were the ensemble method [2] and the residue method [3].

All samples were prepared by mixing a KOH solution with monctite (CaHPO_4). The quantities of CaHPO_4 were weighed with precision and added to a KOH solution of known concentration which was allowed to cool down to room temperature.

The thermodynamic equilibrium of every sample was verified by X-ray analysis. Equilibrium at 25°C was reached after a period of continuous shaking

varying between several days and one month, depending on the proportion of KOH. When equilibrium had been reached, the solution and solid were separated by filtration and analysed.

The methods used for the determination of the different ions were as follows: gravimetric analysis for K^+ [4], UV-visible spectroscopy method for HPO_4^{2-} [5] and complexometric titration with EDTA for Ca^{2+} [6]. Measurement of the pH of the solution allowed the determination of OH^- and H_3O^+ concentrations.

All reagents were of analytical grade (Merck), and decarbonated distilled water was used throughout.

Experimental results

The compositions of samples were expressed in Janěcke coordinates [7]:

$$X = \frac{200[Ca^{2+}]}{P}, \quad U = \frac{100[OH^-]}{P}, \quad V = \frac{200[HPO_4^{2-}]}{P}, \quad Z = \frac{100[H_2O]}{P}$$

with $P=2[Ca^{2+}]+[K^+]$

Table 1 shows the composition of each prepared mixture. It should be noted that the representative point of a sample corresponds to the vectorial sum of X , U and V with the scale indicated in Fig. 1. Thus, the points of mixtures are situated on the section line $CaHPO_4$ –KOH.

Table 1 Compositions of samples prepared from $CaHPO_4$, KOH and H_2O (Janěcke coordinates)

| | X | V | U | Z |
|-----|-------|-------|-------|------|
| b1 | 94.88 | 94.88 | 5.74 | 2276 |
| b2 | 87.10 | 87.10 | 12.87 | 2083 |
| b3 | 74.40 | 74.40 | 24.21 | 2132 |
| b4 | 63.80 | 63.80 | 35.96 | 2051 |
| b5 | 55.22 | 55.22 | 44.78 | 2052 |
| b6 | 34.89 | 34.89 | 65.14 | 1944 |
| b7 | 16.97 | 16.97 | 83.11 | 1933 |
| b8 | 10.33 | 10.33 | 89.66 | 350 |
| b9 | 10.28 | 10.28 | 93.11 | 324 |
| b10 | 10.25 | 10.25 | 89.76 | 395 |
| b11 | 10.13 | 10.13 | 89.91 | 443 |
| b12 | 8.87 | 8.87 | 91.12 | 1024 |
| b13 | 8.69 | 8.69 | 91.35 | 1930 |

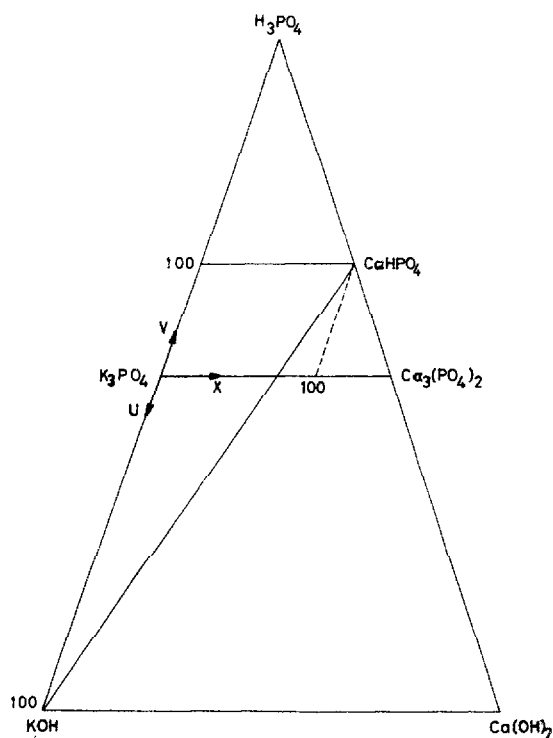


Fig. 1 Scales used in the study of the section $\text{CaHPO}_4\text{-KOH-H}_2\text{O}$ in the system $\text{H}_3\text{PO}_4\text{-KOH-Ca(OH)}_2\text{-H}_2\text{O}$

The composition of solutions at equilibrium were also expressed in Janécke coordinates, taking into account that the concentration of HPO_4^{2-} depends on the pH:

$$X = \frac{200[\text{Ca}^{2+}]}{P}, \quad U = \frac{100[\text{OH}^-]}{P}, \quad V = \frac{200[\text{HPO}_4^{2-}]}{P}, \quad Z = \frac{100[\text{H}_2\text{O}]}{P}$$

$$\text{with } P = 2[\text{Ca}^{2+}] + [\text{K}^+] + [\text{H}_3\text{O}^+] = 3[\text{PO}_4^{3-}] + [\text{OH}^-] + 2[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-]$$

The results of chemical analysis and X-ray diffraction are presented in Table 2. It may be noted that for the samples prepared with a high concentration of KOH, the solid products were mixtures of $\text{K}_4\text{Ca}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ and Ca(OH)_2 .

Figure 2 illustrates a $\text{H}_3\text{PO}_4\text{-KOH-Ca(OH)}_2$ diagram, which indicates

- a CaHPO_4 precipitation field corresponding to a weak ratio of KOH,
- a large precipitation field of an apatitic compound with a structure close to the hydroxyapatitic structure,

– at equilibrium, the solid product of sample 11 comprises a mixture of $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$ and an apatitic product.

Table 2 CaHPO_4 , KOH , H_2O isotherm section at 25°C

| | Janěcke coordinates of saturated solutions | | | | Solid phases at equilibrium |
|-----|--|--------|-------|-------|-----------------------------|
| | X | V | Z | pH | |
| b1 | 5.99 | 110.66 | 41134 | 6.35 | CaHPO_4 |
| b2 | 2.16 | 129.83 | 17904 | 6.57 | Apatitic product |
| b3 | 1.11 | 102.93 | 8965 | 7.40 | |
| | X | U | Z | pH | |
| b4 | 0.00 | 0.84 | 7266 | 11.75 | Apatitic product |
| b5 | 0.56 | 20.67 | 5550 | 13.07 | |
| b6 | 0.00 | 59.06 | 4280 | 13.72 | |
| b7 | 0.00 | 89.42 | 2953 | 13.93 | 4.1.5 |
| b8 | 0.00 | 97.92 | 522 | 14.00 | |
| b9 | 1.15 | 96.58 | 573 | 14.00 | + |
| b10 | 0.00 | 97.92 | 588 | 14.00 | Ca(OH)_2 |
| b11 | 0.4 | 94.33 | 828 | 14.00 | 1.1.1+Ap. |
| b12 | 0.51 | 93.49 | 1356 | 14.00 | Apatitic product |
| b13 | 0.00 | 91.52 | 3406 | 14.00 | |

Ap.: Substituted apatite

4.1.5: $\text{K}_4\text{Ca}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$

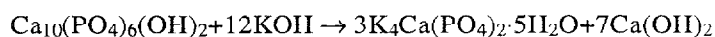
1.1.1: $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$

Discussion

A major part of the solubility sheet is largely superimposed on the system K_2HPO_4 – KOH – H_2O . Nevertheless, for samples b1, b2 and b3, the isocontent water curves do not have the same projection, since in this part the sheet is not planar.

The precipitation field of $\text{K}_3\text{CaH}(\text{PO}_4)_2$, which is defined by three points ($X=32.8$ – $V=16.8$; $X=0$ – $V=32.3$ and $X=0$ – $V=0$), does not appear in the crystallization diagram. These results are explained by the quantity of water in the mixture and the incongruent solubility of this salt, as observed previously [1].

For mixtures with high concentrations of KOH , the solid obtained at equilibrium is a mixture of Ca(OH)_2 and $\text{K}_4\text{Ca}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ according to the reaction



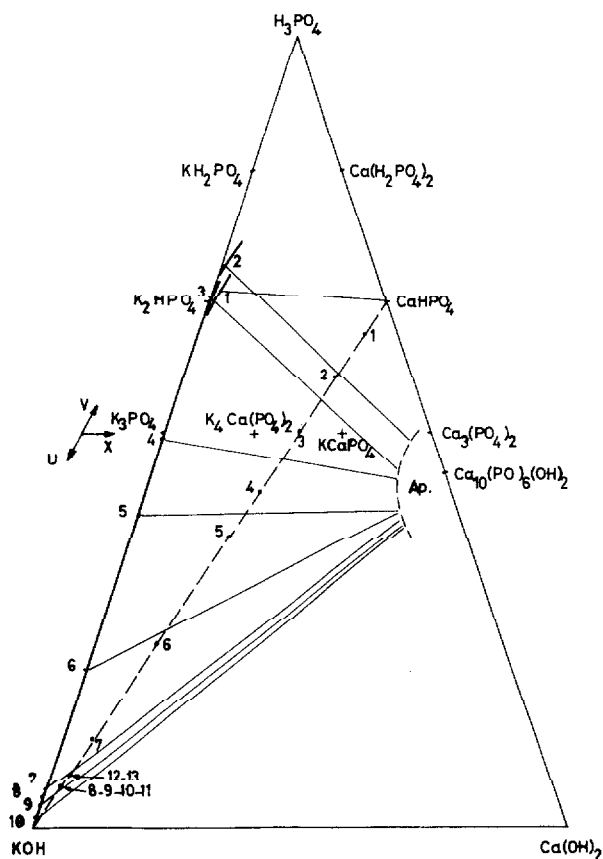
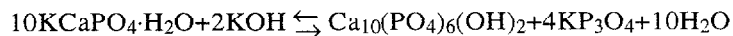
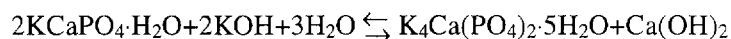


Fig. 2 25°C isotherm of the section $\text{CaHPO}_4\text{-KOH-H}_2\text{O}$ of the system $\text{H}_3\text{PO}_4\text{-KOH-Ca(OH)}_2\text{-H}_2\text{O}$ (the crosses + indicate the positions of $\text{KCaPO}_4\cdot\text{H}_2\text{O}$ and $\text{K}_4\text{Ca(PO}_4)_2\cdot 5\text{H}_2\text{O}$)

The presence of a mixed phosphate $\text{KCaPO}_4\cdot\text{H}_2\text{O}$ in the solid of sample 11 is not surprising, considering the results obtained from the solubility diagram $\text{Ca}_3(\text{PO}_4)_2\text{-K}_3\text{PO}_4\text{-H}_2\text{O}$ [8]. It should be noted that the water content of sample 11 is located between those of the mixtures giving equilibria with apatite and with $\text{K}_4\text{Ca(PO}_4)_2\cdot 5\text{H}_2\text{O}$ and Ca(OH)_2 ; this observation suggests that the precipitation field of $\text{KCaPO}_4\cdot\text{H}_2\text{O}$ is situated between the domains of apatite (with high water content) and $\text{K}_4\text{Ca(PO}_4)_2\cdot 5\text{H}_2\text{O}$ (with low water content).

The following transformation reactions are possible during the crossing from one field to the other:





When these results and the solubility of KOH [9] are taken into consideration, it is possible to give a more complete representation of the precipitation fields of different salts in the part of the system delimited by K_3PO_4 – $\text{Ca}_3(\text{PO}_4)_2$ – KOH – $\text{Ca}(\text{OH})_2$ – H_2O , as shown in Fig. 3.

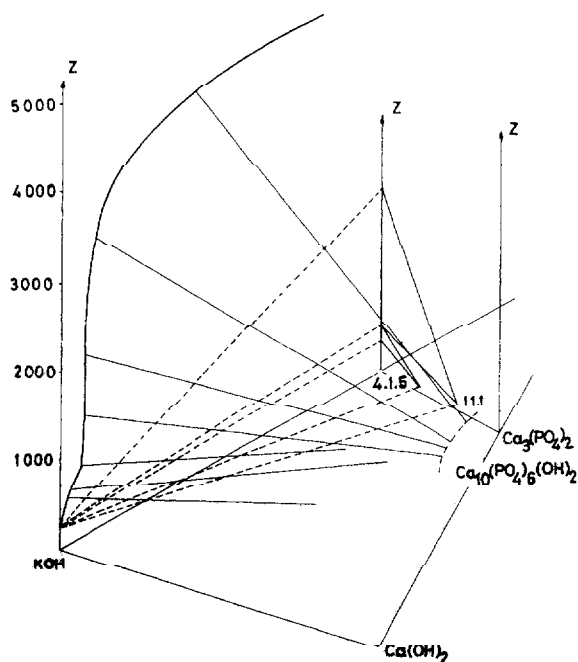


Fig. 3 Spatial representation of the system delimited by H_3PO_4 – KOH – $\text{Ca}(\text{OH})_2$ – H_2O

The results obtained in earlier studies of the systems $\text{Ca}(\text{H}_2\text{PO}_4)_2$ – KOH – H_2O [1] and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ – KH_2PO_4 – H_3PO_4 – H_2O [10], on the nature of the solid compounds obtained at equilibrium, and the results obtained in the present work, agree in confirming the important role of the water content. The nature of the phosphate precipitated in this domain depends on the content of water and the duration of mixing.

It may also be noted that the kinetics of the reaction permit the formation of $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$ and $\text{K}_4\text{Ca}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ more rapidly from a mixture of $\text{KCaPO}_4 \cdot \text{H}_2\text{O}$, $\text{K}_4\text{Ca}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ and KOH in aqueous medium than from a mixture of K_3PO_4 – $\text{Ca}_3(\text{PO}_4)_2$ and H_2O . The time required to reach equilibrium was lower than 1 month, instead 6 months when the starting compounds were $\text{Ca}_3(\text{PO}_4)_2$, K_3PO_4 and water [8].

Conclusions

Study of the section $\text{CaHPO}_4\text{--KOH--H}_2\text{O}$ of the system $\text{H}_3\text{PO}_4\text{--KOH--Ca(OH)}_2\text{--H}_2\text{O}$ has revealed the precipitation field of apatitic products and the coprecipitation field of $\text{KCaPO}_4\cdot\text{H}_2\text{O}$ and $\text{K}_4\text{Ca(PO}_4)_2\cdot 5\text{H}_2\text{O}$ with Ca(OH)_2 . Moreover, this study has demonstrated the influence of the water content on the nature of the product obtained. It has also been found that the formation of $\text{KCaPO}_4\cdot\text{H}_2\text{O}$ and $\text{K}_4\text{Ca(PO}_4)_2\cdot 5\text{H}_2\text{O}$ is more rapid when the phosphate used in the preparation of the samples is CaHPO_4 rather than $\text{Ca}_3(\text{PO}_4)_2$.

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