# A New Calcium Nitrate Phosphate, $CaH_2NO_3PO_4 \cdot H_2O$

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A new salt, $CaH_2NO_3PO_4 \cdot H_2O$, was observed as a solid phase in the system $CaO-N_2O_5-P_2O_5-H_2O$ at 25° and 50° C. The regions of stability and the optical and x-ray characteristics of the salt are reported.

The sulfur shortage, together with recent advances in methods for the production of concentrated nitric acid, has revived interest in fertilizer processes in which phosphate rock is dissolved in nitric acid.

When phosphate rock was dissolved in reagent (70%) nitric acid and the filtered extract was allowed to evaporate slowly at 50° to 60° C., a new salt was formed. Although the crystals appeared to be morphologically very similar to $Ca(H_2PO_4)_2 \cdot H_2O$, the microscopic and x-ray properties differed from those of each of the solid phases that have been reported in the system $CaO-N_2O_5-P_2O_5-H_2O$ (Belopolskii et al., 1937a,b; Flatt et al., 1954, 1956; Plusje, 1948).

Further study of the crystallization process showed that the first phase to crystallize was $Ca(H_2PO_4)_2 \cdot H_2O$. As the mixture thickened to a paste, the first crystals dissolved, crystals of the new salt appeared, and slow drying at 60° to 65° C. produced a mixture of the new salt and anhydrous $Ca(NO_3)_2$. When the paste was dried rapidly at temperatures above 100° C., however, the product was a mixture of $CaHPO_4$ and $Ca(NO_3)_2$. Homogeneous, well crystallized samples of the new salt, prepared from reagent chemicals by two different methods, had compositions (Table I) close to that of $CaH_2NO_3PO_4 \cdot H_2O$.

The salt $CaH_2NO_3PO_4 \cdot H_2O$ precipitates as triclinic blades or tablets that resemble $Ca(H_2PO_4)_2 \cdot H_2O$ in form and habit but have refractive indices $N_\alpha = 1.480$, $N_\beta = 1.542$, and $N_\gamma = 1.580$ which differ considerably from those of monocalcium phosphate monohydrate. The crystals are biaxial (−) with a $2V$ of 75° (measured) or 73° (calculated). The density calculated from the refractive indices and composition (Larsen and Berman, 1943) is 2.26 grams per cc. The x-ray diffraction data are listed in Table II.

The composition and crystallographic form of the new salt suggest that it belongs to the series of substituted monocalcium phosphates (Brown et al., 1958). These are structures of rigid, parallel $Ca-PO_4$ sheets separated by regions of relatively low atomic density that are occupied by the hydrate water and half of the phosphate ions. It is in these regions that substitutions of alkali ions for hydrogen and of other anions for phosphate occur. In this type of substitution some variation in composition is to be expected. As with other compounds in the series of substituted monocalcium phosphates, the substitution of nitrate for phosphate frequently is incomplete, and the composition differs slightly from that of the stoichiometric salt. Crystallographic studies are being made of the new salt to determine its general structural features.

The published data (Belopolskii et al., 1937a, b; Flatt et al., 1956; Plusje, 1948) for the system $CaO-N_2O_5-P_2O_5-H_2O$ include no stability region for $CaH_2NO_3-PO_4 \cdot H_2O$, even though the solution compositions in which the new salt appears are included in the regions studied by the earlier investigators. The solid phases were identified in these earlier studies, however, only by the morphology of the crystals in their mother liquor, and the new compound is indistinguishable from monocalcium phosphate monohydrate under these conditions. Anhydrous monocalcium phosphate also was not reported as a solid phase in the system by the earlier investigators, apparently for the same reason. In the three-component system $CaO-P_2O_5-H_2O$, $Ca(H_2PO_4)_2$ forms prismatic or rod crystals, but in the presence of nitric acid it forms plate crystals whose morphology and interfacial angles are very similar to those of $Ca(H_2PO_4)_2 \cdot H_2O$, indicating a structural similarity between the anhydrous salt and the monohydrate. Hence, the identification of these compounds on the basis of their morphology is unreliable.

### Table I. Preparations of $CaH_2NO_3PO_4 \cdot H_2O$

| | Composition, % | | | | Moles/Mole P₂O₅ | | |
| | CaO | N₂O₅ | P₂O₅ | H₂O (diff.) | CaO | N₂O₅ | H₂O |
|---|---|---|---|---|---|---|---|
| Sample I | 25.9 | 21.6 | 32.5 | 20.0 | 2.02 | 0.87 | 4.85 |
| Sample II | 25.6 | 22.4 | 32.7 | 19.3 | 1.98 | 0.90 | 4.65 |
| Stoichiometric | 25.83 | 24.88 | 32.69 | 16.60 | 2.00 | 1.00 | 4.00 |

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### Table II. X-Ray Diffraction Pattern of $CaH_2NO_3PO_4 \cdot H_2O$

Scanned at 0.25° $2\theta$/min. Intensities read from goniometer tracings and reported as per cent of strongest line

| d, A. | I | d, A. | I | d, A. | I |
|---|---|---|---|---|---|
| 15.2 | 26 | 3.10 | 5 | 2.40 | 5 |
| 10.3 | 7 | 2.90 | 7 | 2.38 | 5 |
| 9.30 | 100 | 2.86 | 9 | 2.30 | 3 |
| 5.75 | 5 | 2.83 | 8 | 2.16 | 10 |
| 5.09 | 6 | 2.75 | 5 | 2.13 | 10 |
| 4.30 | 28 | 2.65 | 3 | 1.94 | 3 |
| 3.83 | 11 | 2.59 | 6 | 1.92 | 6 |
| 3.66 | 14 | 2.55 | 16 | 1.90 | 6 |
| 3.18 | 45 | 2.49 | 5 | 1.86 | 5 |
| 3.14 | 4 | | | | |

To define the region of stability of $CaH_2NO_3PO_4 \cdot H_2O$, studies were made of the system $CaO-N_2O_5-P_2O_5-H_2O$ at $25.0° \pm 0.1°$ C. and $50.0° \pm 0.5°$ C. The equilibration mixtures were prepared from reagent chemicals and, to ensure that equilibrium had been obtained, at least two mixtures on different sides of equilibrium were prepared for each ternary point, and four mixtures were prepared for each invariant point at which $CaH_2NO_3PO_4 \cdot H_2O$ was a stable solid phase. At each temperature, the mixtures were equilibrated for at least 2 months, and for 4 to 5 months when the mixtures were markedly viscous. During the equilibration period, the mixtures were shaken

periodically and the solid phases were examined petrographically to be certain that the desired solid phases were maintained. Samples for analysis of the liquid phase were filtered on a fritted-glass funnel. The 50° C. samples were filtered in a water-jacketed funnel into a receiving flask that was maintained at 50° C. in a water bath.

The chemical analyses and solid phase compositions are shown in Table III, together with data for phase-boundary solutions that have been reported previously (Bassett, 1908; Bassett and Taylor, 1912; Elmore and Farr, 1940; Flatt et al., 1954). Samples 11 at 25° C. and 30 at 50° C. contained 2.5 and 8%, respectively, of the total phosphate as pyrophosphate, showing that these regions of the system are more complex than a four-component system; these equilibration mixtures were prepared with superphosphoric acid to obtain the desired $P_2O_5$ content.

### Table III. The System $CaO-N_2O_5-P_2O_5-H_2O$

| No. | CaO | N₂O₅ | P₂O₅ | H₂O | Solid Phase[a] |
|-----|-----|------|------|-----|----------------|
| | Composition of Saturated Solution, Wt. % | | | | |

Results at 25° C.

| No. | CaO | N₂O₅ | P₂O₅ | H₂O | Solid Phase[a] |
|-----|-----|------|------|-----|----------------|
| 1 | 12.9 | 39.3 | 18.1 | 29.8 | CNA, CN2, CNP |
| 2 | 16.1 | 38.0 | 15.6 | 30.3 | CN2, CN3, CNP |
| 3 | 16.1 | 34.3 | 16.8 | 32.8 | CN3, CN4, CNP |
| 4 | 19.5 | 36.7 | 1.3 | 42.4 | CN4, MCPM, DCP |
| 5 | 14.8 | 32.5 | 17.7 | 35.0 | CN4, CNP, MCPM |
| 6 | 6.0 | 20.4 | 36.9 | 36.7 | CNP, MCPA, MCPM |
| 7 | 3.2 | 20.4 | 44.7 | 31.7 | CNA, CNP, MCPA |
| 8[b] | 3.5 | 62.2 | 0.0 | 34.3 | CNA, CN2 |
| 9[b] | 10.0 | 46.1 | 12.3 | 31.6 | CNA, CN2 |
| 10 | 4.76 | 27.6 | 35.5 | 32.1 | CNA, CNP |
| 11 | 1.0 | 18.6 | 51.9 | 28.4 | CNA, MCPA |
| 12[b] | 9.2 | 55.9 | 0.0 | 34.9 | CN2, CN3 |
| 13[b] | 13.8 | 45.2 | 8.5 | 32.5 | CN2, CN3 |
| 14 | 15.8 | 36 4 | 16 1 | 31.7 | CN3, CNP |
| 15[b] | 12.0 | 51.5 | 0.0 | 36.5 | CN3, CN4 |
| 16[b] | 13.9 | 42.7 | 8.2 | 35.2 | CN3, CN4 |
| 17 | 7.9 | 23.5 | 32.1 | 36.5 | CNP, MCPM |
| 18 | 2.7 | 12.9 | 45.0 | 39.4 | MCPA, MCPM |
| 19[c] | 0.2 | 0.0 | 62.6 | 37.2 | MCPA, MCPM |
| 20 | 11.9 | 20.1 | 7.1 | 61.0 | MCPM, DCP |
| 21[c] | 5.8 | 0.0 | 24.1 | 70.1 | MCPM, DCP |

Results at 50° C.

| No. | CaO | N₂O₅ | P₂O₅ | H₂O | Solid Phase[a] |
|-----|-----|------|------|-----|----------------|
| 22 | 26.3 | 49.7 | 0.93 | 23.1 | CNA, CN3, CNP |
| 23 | 25.0 | 46.6 | 1.09 | 27.3 | CN3, CNP, DCP |
| 24 | 23.7 | 44.0 | 2.01 | 30.3 | CNP, MCPM, DCP |
| 25 | 9.24 | 30.7 | 27.2 | 32.9 | CNA, CNP, MCPA |
| 26 | 13.6 | 28.6 | 23.1 | 34.7 | CNP, MCPA, MCPM |
| 27 | 20.8 | 42.8 | 10.5 | 26.0 | CNA, CNP |
| 28 | 7.25 | 27.9 | 34.2 | 30.6 | CNA, MCPA |
| 29 | 4.25 | 24.8 | 40.2 | 30.7 | CNA, MCPA |
| 30 | 1.69 | 13.0 | 57.2 | 28.1 | CNA, MCPA |
| 31 | 1.45 | 11.0 | 61.2 | 26.4 | CNA, MCPA |
| 32 | 16.9 | 35.2 | 15.5 | 32.4 | CNP, MCPM |
| 33 | 4.67 | 11.9 | 44.7 | 38.8 | MCPA, MCPM |
| 34 | 3.41 | 8.9 | 48.9 | 38.9 | MCPA, MCPM |
| 35[d] | 0.34 | 0.0 | 62.01 | 37.65 | MCPA, MCPM |
| 36 | 20.7 | 39.5 | 2.76 | 37.0 | MCPM, DCP |
| 37 | 11.4 | 17.8 | 13.4 | 57.4 | MCPM, DCP |
| 38[d] | 5.73 | 0.0 | 29.61 | 64.66 | MCPM, DCP |
| 39[e] | 26.6 | 51.3 | 0.0 | 22.1 | CN2 |
| 40[e] | 25.2 | 48.6 | 0.0 | 26.2 | CN3 |

[a] CNA = $Ca(NO_3)_2$
CN2 = $Ca(NO_3)_2 \cdot 2H_2O$
CN3 = $Ca(NO_3)_2 \cdot 3H_2O$
CN4 = $Ca(NO_3)_2 \cdot 4H_2O$
CNP = $CaH_2NO_3PO_4 \cdot H_2O$
MCPM = $Ca(H_2PO_4)_2 \cdot H_2O$
MCPA = $Ca(H_2PO_4)_2$
DCP = $CaHPO_4$
[b] From Flatt et al. (1954).
[c] From Elmore and Farr (1940).
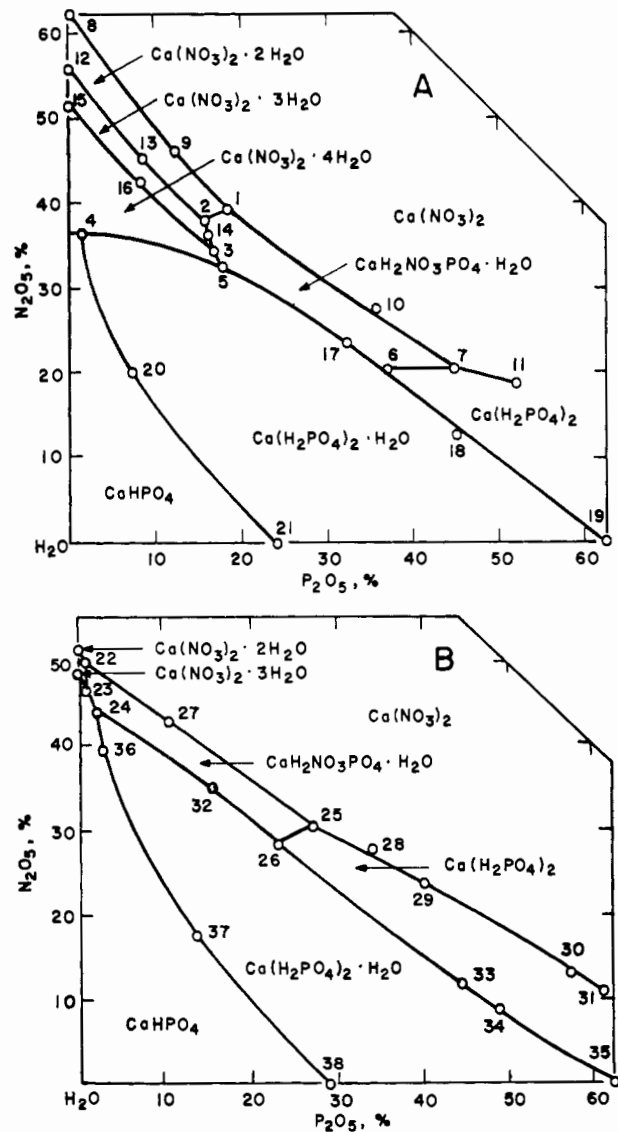[d] From Bassett and Taylor (1912).
[e] From Bassett (1908).



Figure 1. The system $CaO-N_2O_5-P_2O_5-H_2O$, projected on the $N_2O_5-P_2O_5-H_2O$ face

A. At 20° C. B. At 50° C. Numbers on points are those in Table III

The data are projected on the $N_2O_5$–$P_2O_5$–$H_2O$ face of the system in Figure 1 to show the relationship of the various fields. The solution compositions along the isotherms agree reasonably well with those reported by Flatt et al. (1954, 1956) except for the region of high viscosity at 25° C. (38 to 39% $N_2O_5$, 16 to 18% $P_2O_5$) in which the solutions are much more concentrated with respect to $Ca(NO_3)_2$ than those reported by Flatt. The disagreement at 50° C. is in the region of compositions that contain 45 to 52% $N_2O_5$ and less than 5% $P_2O_5$, and in which the high viscosity of the solutions makes equilibration to the stable hydrate of calcium nitrate very difficult. In the present study, the solid calcium nitrate was always the trihydrate, but seed crystals of the dihydrate that were added to these mixtures neither eroded nor dissolved, nor did they appear to grow.

To be certain that both hydrates of calcium nitrate are stable at 50° C., melting points were determined on well dried, optically homogeneous samples of the two hydrates. The dihydrate, $Ca(NO_3)_2 \cdot 2H_2O$, melted at 52.5° C. with decomposition to a solution phase and a solid phase of $Ca(NO_3)_2$. The trihydrate melted at 51.4° C. which compares well with the published value of 51.1° C. obtained in a study (Bassett and Taylor, 1912) that showed $Ca(NO_3)_2 \cdot 2H_2O$ as a stable phase in the system $CaO$–$N_2O_5$–$H_2O$ at 50° C. At equilibrium, both hydrates probably occupy a region of this small area at 50° C. Above 52.5° C., neither salt would be present and the fields of $CaHPO_4$ and $Ca(NO_3)_2$ would join, as reported by Flatt et al. (1956).

DISCUSSION

Examination of Figure 1 shows that the fields of stability of $CaH_2NO_3PO_4 \cdot H_2O$ and $Ca(H_2PO_4)_2$ are included in the field assigned to $Ca(H_2PO_4)_2 \cdot H_2O$ by the earlier investigators. Comparison of $A$ and $B$ shows that at the lower temperature there is an increase in the area occupied by the hydrates of calcium nitrate and a decrease in the areas occupied by dicalcium phosphate and anhydrous monocalcium phosphate. These changes result in a shift of the $CaH_2NO_3PO_4 \cdot H_2O$ field toward the direction of higher $P_2O_5$ content. Part of the field assigned to $CaHPO_4$ at 25° C. can be occupied by $CaHPO_4 \cdot 2H_2O$, but this part would be very small, as explained by Elmore and Farr (1940), and so was not investigated in this study. The hydrate of dicalcium phosphate is not stable at 50° C.

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