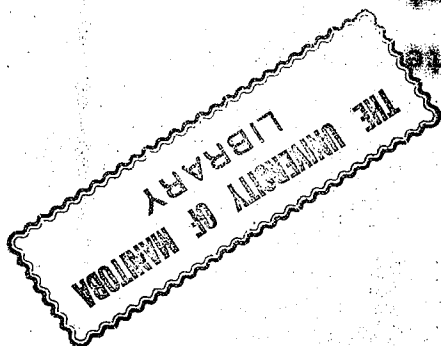


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John Wallace Coates

BY

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A PHASE RULE STUDY OF THE QUATERNARY SYSTEM

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I INTRODUCTION

Introduction

A thorough understanding of the quaternary system $\text{CaO} - \text{P}_2\text{O}_5 - \text{SO}_3 - \text{H}_2\text{O}$ is of considerable importance in the manufacture of phosphoric acid and certain fertilizers, known as "superphosphates". Superphosphate fertilizer is made by the action of sulphuric acid on phosphate rock or bone, and usually results (32) in a mixture of monocalcium phosphate monohydrate (Table I) and anhydrous calcium sulphate (anhydrite). "Double" or "triple" superphosphates are made by treating phosphate rock or bone with phosphoric, rather than sulphuric, acid. In this fertilizer anhydrous monocalcium phosphate is believed to be the predominant phosphate (32).

If more sulphuric acid is used, as is done in the phosphoric acid industry, the P_2O_5 content of the rock is entirely converted to free phosphoric acid.

In addition to monocalcium phosphate, which occurs in superphosphate, other calcium salts of orthophosphoric acid (H_3PO_4) are known, and those which are capable of existence in neutral or acid solutions are indicated in Table I. Calcium phosphates having higher $\text{CaO}/\text{P}_2\text{O}_5$ ratios are claimed, but these are known only in alkaline regions which were not considered in this study. Two systems of nomenclature are commonly used, and both are indicated in Table I. Throughout this paper, however,

the more common system, indicated in column three, is used. By this system the salts are named "monocalcium", "dicalcium" and "tricalcium" according as the ratio CaO/P_2O_5 in the salt is equal to one, two or three.

Table I

The calcium salts of H_2PO_4

Formula	Ratio:	Orthophosphate	Calcium
$Ca(H_2PO_4)_2$	$CaO \cdot P_2O_5 \cdot 2H_2O$	Monocalcium	Dihydrophosphate
$Ca(H_2PO_4)_2 \cdot H_2O$	$CaO \cdot P_2O_5 \cdot 3H_2O$	Monocalcium	monohydrate
$CaHPO_4$	$2CaO \cdot P_2O_5 \cdot H_2O$	Dicalcium	Monohydrophosphate
$CaHPO_4 \cdot 2H_2O$	$2CaO \cdot P_2O_5 \cdot 3H_2O$	Dicalcium	dihydrate
$Ca_3(PO_4)_2$	$3CaO \cdot P_2O_5$	Tricalcium	Phosphate
$Ca_3(PO_4)_2 \cdot H_2O$	$3CaO \cdot P_2O_5 \cdot H_2O$	Tricalcium	monohydrate

The common calcium sulphates are:

- (1) $CaSO_4$ - anhydrite or β -calcium sulphate.
- (2) $CaSO_4$ - "soluble anhydrite", "dehydrated hemihydrate" or γ - $CaSO_4$
- (3) $CaSO_4 \cdot \frac{1}{2}H_2O$ - hemihydrate or "Plaster of Paris".
- (4) $CaSO_4 \cdot 2H_2O$ - gypsum.

Investigation had to be abandoned.

but for reasons to be pointed out later, this phase of the investigation, to determine whether such solid solution exists, in a reduced yield of $H_2PO_4^-$. It was hoped, as a part of this solid solution formation between these compounds, resulting commercial manufacturer (16) of phosphoric acid also suspects or double salts between $CaHPO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 2H_2O$. A $SO_3 - H_2O$ have suspected the formation of solid solution Various workers (52 and 53) in the system $CaO - P_2O_5 - SO_3$ of the various phosphates and sulphates of calcium at 75.5° to determine the regions of stability and solubility curves. This investigation was therefore undertaken in order acid industries.

practical temperature with respect to the fertilizer and it has never been investigated hitherto at 75° , a more the four component system $CaO - P_2O_5 - SO_3 - H_2O$ at 25° , although Cameron and Hill (13) have investigated of each.

to know the region of stability and the solubility curve and its acid concentration. It therefore becomes important contact with a given solution, depending upon its temperature of calcium phosphates and sulphates which may exist in It is evident, then, that there is a wide selection to (46), but this does not form below 1195° .

A third anhydrous form, $\gamma - CaSO_4$ has been referred

THEORETICAL CONSIDERATIONS