

NATIONAL BUREAU OF STANDARDS REPORT

10 072

Progress Report
on
SOLUBILITY OF CALCIUM HYDROGEN PHOSPHATE
AT 5, 15, 25 AND 37°C



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards¹ was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in four broad program areas. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Radiation Research, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Measurement Services and the following technical divisions:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic and Molecular Physics—Radio Physics²—Radio Engineering²—Time and Frequency²—Astrophysics²—Cryogenics.²

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; develops, produces, and distributes standard reference materials; relates the physical and chemical properties of materials to their behavior and their interaction with their environments; and provides advisory and research services to other Government agencies. The Institute consists of an Office of Standard Reference Materials and the following divisions:

Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations in the development of technological standards, and test methodologies; and provides advisory and research services for Federal, state, and local government agencies. The Institute consists of the following technical divisions and offices:

Engineering Standards—Weights and Measures—Invention and Innovation—Vehicle Systems Research—Product Evaluation—Building Research—Instrument Shops—Measurement Engineering—Electronic Technology—Technical Analysis.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center consists of the following divisions:

Reactor Radiation—Linac Radiation—Nuclear Radiation—Applied Radiation.

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in the selection, acquisition, and effective use of automatic data processing equipment; and serves as the principal focus for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

Information Processing Standards—Computer Information—Computer Services—Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System, and provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

¹ Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted, mailing address Washington, D.C. 20234.
² Located at Boulder, Colorado 80302.

³ Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

311.05-11-3110561

June 30, 1969

NBS REPORT

10 072

Progress Report

on

SOLUBILITY OF CALCIUM HYDROGEN PHOSPHATE AT 5, 15, 25 AND 37°C

by

H. McDowell,* J. R. Sutter,[†] and W. E. Brown*

* Research Associates from the American Dental Association
in the Dental Research Section, National Bureau of Standards,
Washington, D. C. 20234

[†] Assoc. Professor of Chemistry, Howard University, Washington, D. C.
This investigation was supported in part by Research Grants
DE-00572 to the American Dental Association from the
National Institute of Dental Research, and is part of the
dental research program conducted by the National Bureau
of Standards in cooperation with the Council on Dental Re-
search of the American Dental Association; the Dental Re-
search Division of the U. S. Army Medical Research and
Development Command; the Dental Sciences Division of the
School of Aerospace Medicine, USAF; and the Veterans
Administration.

IMPORTANT NOTICE

NATIONAL BUREAU OF STANDARDS
for use within the Government.
and review. For this reason, the
whole or in part, is not author-
ized to be distributed outside the
Bureau of Standards, Washington,
D. C. The Report has been specifically

Approved for public release by the
Director of the National Institute of
Standards and Technology (NIST)
on October 9, 2015.

as accounting documents intended
subjected to additional evaluation
listing of this Report, either in
the Office of the Director, National
Institute of Standards and Technology
or by the Government agency for which
it was prepared, or by the author for
his own use.



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

Solubility of Calcium Hydrogen Phosphate at
5, 15, 25 and 37°C

ABSTRACT

The solubility of CaHPO_4 has been determined in the ternary system, $\text{Ca}(\text{OH})_2-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$, at 5, 15, 25 and 37°C. The same results are obtained when equilibrium is approached from super- and under-saturation. The solubility product constant, $K_{\text{sp}} = (\text{Ca}^{2+})(\text{HPO}_4^{2-})$, varies with pH unless formation of ion pairs CaHPO_4^0 and $\text{CaH}_2\text{PO}_4^+$ is taken into account. Solubility product constants and standard errors for CaHPO_4 are $1.97 \pm 0.03 \times 10^{-7}$, $1.64 \pm 0.01 \times 10^{-7}$, $1.25 \pm 0.01 \times 10^{-7}$ and $0.94 \pm 0.01 \times 10^{-7}$ at 5, 15, 25 and 37°C, respectively. Association constants and standard errors are 243 ± 32 , 187 ± 24 , 377 ± 37 and 355 ± 62 for CaHPO_4^0 and 5.2 ± 0.7 , 9.6 ± 0.6 , 9.6 ± 0.7 and 8.1 ± 0.6 for $\text{CaH}_2\text{PO}_4^+$ at the same respective temperatures. Thermodynamic functions for the dissolution reaction for CaHPO_4 and the association reactions for CaHPO_4^0 and $\text{CaH}_2\text{PO}_4^+$ are also presented.

SOLUBILITY OF CALCIUM HYDROGEN PHOSPHATE AT
5, 15, 25 AND 37°C (1)

(1) This paper is based on a dissertation submitted by H. McDowell to the faculty of Howard University in partial fulfillment of the requirements for the Ph. D. degree

by Hershel McDowell, Walter E. Brown,

Research Associates, American Dental Association, National

Bureau of Standards, Washington, D. C. 20234 .

and John R. Sutter,

Department of Chemistry, Howard University, Washington, D. C.

20001.

INTRODUCTION

Anhydrous dicalcium phosphate, CaHPO_4 , is a stable phase in the system, $\text{Ca}(\text{OH})_2-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$. Accurate information about the solubility of CaHPO_4 is of great value in establishing its stability range, in determining its thermodynamic properties, and in understanding interrelations among the calcium phosphates that precipitate from aqueous solutions.

Two values are given in the literature for the apparent solubility product of CaHPO_4 at 25°C(2, 3) but these are not

(2) T. D. Farr, Tenn. Valley Authority, Chem. Eng. Rept. No. 8, Wilson Dam, Ala., (1950).

(3) K. L. Elmore, and T. D. Farr, Ind. Eng. Chem. 32, 580 (1940).

in good agreement. It is now known that the apparent solubility products for calcium phosphates vary with the equilibrium pH if they are calculated without taking into account ion-pair formation (4). The neglect of ion-pair formation at rela-

(4) E. C. Moreno, T. M. Gregory and W. E. Brown, J. Res. NBS 70A (Phys. and Chem.) No. 6, 545 (1966).

tively high concentrations probably accounts for much of the discrepancy in the reported values.

In this paper, we report the solubilities of CaHPO_4 at four temperatures in the dilute range of the phase diagram for this system. Three different experimental conditions were used to minimize effects due to metastability of CaHPO_4 with respect to other calcium phosphates, and to ascertain that equilibrium was reached. Solubility products and standard heat and entropy of the dissolution reaction for CaHPO_4 and association constants and standard heats and entropies of association for the ion pairs, CaHPO_4° and $\text{CaH}_2\text{PO}_4^+$, are reported for 5, 15, 25 and 37°C. Equilibrations were made in the ternary system to avoid complications in the interpretation of data which might result from the presence of other ions.

EXPERIMENTAL SECTION

Chemicals. The CaHPO_4 was prepared by dehydration of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was prepared in pure, well crystallized form by ammoniating an aqueous solution, initially saturated with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, in an ice bath. The dehydration was accomplished by boiling 400 g of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in 4 ℓ of 0.07M phosphoric acid for 72 hours. The solid was collected by filtration and washed with small volumes of distilled water until the pH of the wash solution reached 6.0. The solid was then washed thoroughly with acetone and dried in vacuo (3 hours at 80°C , then 60 hours at 50°C). Examination with a petrographic microscope indicated that (a) refractive indices of this solid matched those reported for CaHPO_4 (2), (b) the material was free of extraneous phases, and (c) the individual $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ crystals had converted into multicrystalline CaHPO_4 with an average domain size of about 20 μm . The calcium and phosphorus contents and the mean errors were $29.49 \pm 0.10\%$ (theoretical, 29.46) and $22.71 \pm 0.06\%$ (theoretical, 22.71), respectively.

Doubly-crystallized phosphoric acid hemihydrate, $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, was used to prepare a 1 M stock solution. Other acid solutions were prepared by diluting the stock solution with freshly-boiled distilled water and standardized by chemical analysis.

Analyses. Phosphorus was determined spectrophotometrically using the molybdoavanadate reagent of Brabson, et al (5).

(5) J. A. Brabson, R. L. Dunn, E. A. Epps, Jr., W. M. Huffman, and K. D. Jacob, J. Assoc. Anal. Chem. 41, 517 (1958).

Standard phosphorus solutions were prepared from primary standard KH_2PO_4 from a commercial source. Absorbance measurements were made with a double beam spectrophotometer. A least squares equation relating the absorbances of the standard solutions to their concentrations was used to compute the concentration of phosphorus in the samples. The standard error in this method is about $\pm 1.0\%$ of the phosphorus in the sample.

Calcium was determined with an atomic absorption spectrophotometer equipped with a hollow cathode calcium lamp and a single slot burner. Standard calcium solutions containing a Ca/P weight ratio of 0.5 were prepared from CaCO_3 and reagent grade KH_2PO_4 . The CaCO_3 was

prepared by reprecipitating reagent-grade CaCO_3 three times from hot hydrochloric acid solution with ammonium carbonate solution. Strontium chloride solution was added to each standard to give a strontium concentration of 2.00 mg/ml to suppress interference by phosphate. The samples were diluted to an appropriate calcium concentration and the strontium concentration was made equal to that in the standard solutions. Absorption measurements were made at 4227 Å in an air-acetylene flame. The calcium concentrations in the samples were estimated using a standard curve. The standard error in this method is about $\pm 1.5\%$ of the calcium in the sample. The pH measurements were made with a commercial pH meter equipped with glass and saturated calomel electrodes and standardized with certified National Bureau of Standards buffers. The uncertainty in the pH measurements was estimated to be about ± 0.008 pH units.

Equilibrations. At 25 and 37°C, three types of equilibrations were used: (1) "leaching experiments" in which a dilute phosphoric solution was passed through a column of CaHPO_4 , (2) "batch experiments" in which CaHPO_4 was rotated with dilute phosphoric acid, and (3) "supersaturation experiments" in which a solution supersaturated with respect to CaHPO_4 was passed through a column of the salt. At 5 and 15°C only leaching experiments were used.

The apparatus and technique used in the leaching experiments were essentially the same as those described by Moreno, Gregory and Brown (4). An 8 cm layer of CaHPO_4 , supported in the thermostated column by a medium porosity fritted glass plug, was washed several times with dilute phosphoric acid and was then leached with the same acid. The temperature in the column was controlled within $\pm 0.01^\circ\text{C}$. A leaching rate was selected so that doubling the flow rate would cause no change in the pH of the effluent. Nitrogen was used to keep the solutions free of CO_2 . At least three aliquots of each effluent were taken for calcium and phosphorus analyses.

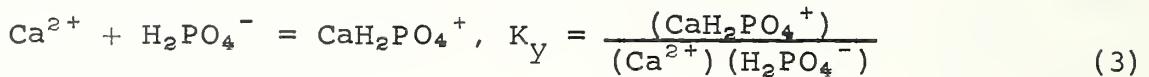
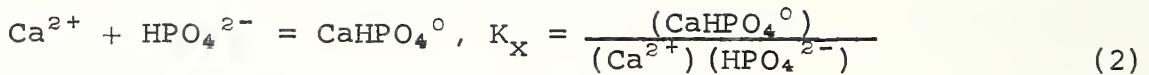
In batch experiments, 4.0 g of CaHPO_4 was added to each of several glass stoppered bottles and washed several times with small volumes of the acid solution with which the solid was to be equilibrated. About 125 ml of the acid was then added and the bottles were sealed with paraffin wax and rotated end-over-end at 7 rpm in a thermostated water bath. In preliminary experiments, lasting up to seven days, it was shown that equilibrium was attained within 24 hours. Thereafter, solutions equilibrated for about 24 hours were filtered using the leaching column, and their pH and calcium and phosphorus concentrations were determined.

To attain equilibrium from supersaturation, solutions supersaturated with respect to CaHPO_4 were passed through a column of this salt in the leaching apparatus. These solutions were prepared by leaching either a column of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at room temperature or a column of CaHPO_4 at a temperature 10°C lower than that at which equilibration experiments were made. The pH and calcium and phosphorus concentrations of the effluent were determined before and after it passed through the column.

Calculations. Initially, "apparent" solubility product constants, K'_{sp} , were calculated by the procedure described by Moreno, et al (4), except that the Davies equation (6)

(6) C. W. Davies, "Ion Association", Butterworths Inc.,
Washington, D. C. 1962, p. 41.

was used to calculate activity coefficients. In the calculation of K'_{sp} , the formation of calcium-phosphate ion pairs was ignored. Subsequently, in the calculation of "true" solubility products, K_{dcA} , allowance was made for ion-pair formation. The equilibria, in addition to those for the dissociation constants of phosphoric acid, are defined by the following equations.



The relationships between the solubility product K_{DCA} and the association constants K_x and K_y follow from the substitution of eq 1 and the second dissociation constant of phosphoric acid into eq 2 and 3.

$$K_x = \frac{(\text{CaHPO}_4^{\circ})}{K_{\text{DCA}}} \quad (4)$$

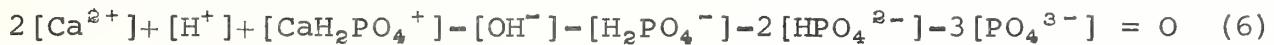
$$K_y = \frac{K_2(\text{CaH}_2\text{PO}_4^+)}{K_{\text{DCA}}(\text{H}^+)} \quad (5)$$

In order to solve the above equations for K_{DCA} , K_x , and K_y , approximate values for these constants K_{sp}° , K_x° and K_y° , were chosen. These values were improved by a least squares adjustment procedure (7) based on the method of Deming (8), which

(7) T. M. Gregory, E. C. Moreno, and W. E. Brown, to be published
(8) W. E. Deming, "Statistical Adjustment of Data", John Wiley and Sons, Inc., New York, 1943, Chapter 4.

simultaneously adjusted the weighted observables: pH, initial phosphoric acid, and final calcium and phosphorus concentrations. In this procedure, the weighted sum of squares was minimized subject to three condition functions based on electroneutrality, solubility product of CaHPO_4 , and congruent dissolution of

the solid, respectively:



$$[\text{M}-\alpha] [\text{P}-\alpha] \frac{f\text{Ca}^{2+}}{\lambda} - K_{\text{sp}}^0 = 0 \quad (7)$$

$$\frac{[\text{M}]}{[\text{P}-\text{P}_0]} - 1 = 0 \quad (8)$$

where (4)

$$\lambda = \frac{(\text{H}^+)^2}{K_1 K_2} + \frac{(\text{H}^+)}{K_2 f_1} + \frac{1}{f_2} + \frac{K_3}{(\text{H}^+) f_3} \quad (9)$$

K_1 (9), K_2 (10) and

K_3 (11) are the first, second and third dissociation constants

(9) L. F. Nims, J. Am. Chem. Soc. 56, 1110 (1934).

(10) R. G. Bates and S. F. Acree, J. Res. NBS 30, 129 (1943)
RP1524.

(11) C. E. Vanderzee and A. S. Quist, J. Phys. Chem. 65, 118
(1961).

of phosphoric acid; f_1 , f_2 and f_3 are the activity coefficients of H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} , respectively; and α , the total concentration of ion pairs in a given solution is given by

$$\alpha = \frac{1}{2}[\text{M}+\text{P}] - \frac{1}{2}\{[\text{M}+\text{P}]^2 - 4[\text{M}\text{P} - \lambda K_{\text{sp}}^0 / f\text{Ca}^{2+}]^{\frac{1}{2}}\} \quad (10)$$

where M and P are the total calcium and phosphorus concentrations. In these equations, parentheses indicate molar activities and brackets indicate molar concentrations.

Ionic strengths were calculated from the equation

$$I = \frac{1}{2} \sum C_i z_i^2 \quad (11)$$

where C_i is the concentration of the i th ion and z_i is its charge. Activity coefficients were calculated using the equation (6)

$$-\log f_i = A_t z_i^2 \left\{ \frac{\frac{1}{I^2}}{1 + \frac{1}{I^2}} - 0.3I \right\} \quad (12)$$

where A_t , a temperature dependent constant, was given the values 0.492, 0.500, 0.509 and 0.521 at 5, 15, 25 and 37°C, respectively (12). The activity coefficient for $\text{CaH}_2\text{PO}_4^+$ was

(12) G. G. Manov, R. G. Bates, W. J. Hamer, and S. F. Acree, J. Am. Chem. Soc. 65, 1765 (1943).

assumed to be equal to that for H_2PO_4^- , and the activity coefficients of uncharged species were assumed to be unity. The calculations were made by a computer using a program incorporating the above procedure (13).

(13) Provided by E. C. Moreno and T. M. Gregory.

RESULTS

Table I summarizes the experimental data and the derived constants for the equilibria approached from undersaturation at four temperatures. The first column gives the compositions

of initial phosphoric acid; the next three columns give the pH and calcium and phosphorus concentrations of the equilibrated solutions. The values in parentheses give the differences between the last significant figures in the experimental and the adjusted values. A negative value indicates that the experimental value is the larger of the two. The adjusted values that differ from the experimental values by more than two times the experimental error are marked with asterisks. The next column gives the percent calcium calculated to be in the form of ion pairs; the next gives the "apparent" solubility product constants calculated without assuming ion-pair formation; and the final column gives the "true" solubility product constants and the ion-pair association constants as defined by equations 1, 2 and 3, respectively.

With few exceptions, the differences between the experimental and adjusted values for the initial acid concentration and final pH and calcium and phosphorus concentrations are within the experimental errors. The errors in the solubility products and association constants are standard errors based on $(qN - b)$ degrees of freedom; where q is the number of condition functions (two for the supersaturation experiments and three for all others), N is the number of equilibrated solutions in the set and b is the number of adjustable parameters.

Table II gives the same information as Table I for the equilibrations from supersaturation, except that pH and calcium concentration before equilibrating with CaHPO_4 are also given. It can be seen that in each instance the pH decreased on equilibration, indicating that precipitation had occurred. The differences between the calcium and phosphorus concentrations before and after equilibration are so small that errors in analyses preclude calculation of the Ca/P ratio of the material that precipitated during equilibration. Since the data in Table II form sets that are indistinguishable from corresponding sets in Table I, we assumed that the precipitate in the equilibrations from supersaturation was CaHPO_4 . This was confirmed by a plot of the chemical potential of $\text{Ca}(\text{OH})_2$ against that of H_3PO_4 (14, 15) which revealed that

(14) E. C. Moreno, W. L. Lindsay, and G. Osborn, *Soil Sci.*, 90, 59 (1960).

(15) K. MacGregor and W. E. Brown, *Nature* 205, 359 (1965).

the Ca/P ratio of the equilibrating phase is 1.000 at both temperatures, 25 and 37° , at which supersaturation experiments were made. The data were treated so that each of the different sets of experiments yielded independent values for the three constants, K_{sp} , K_x and K_y . The weighted means of these constants, as given in Tables I and II, are listed in Table III. In each instance,

the constants given in Tables I and II are within two standard deviations of the over-all mean value. Also given in Table III are the weighted mean values of the constants derived from a treatment in which activity coefficients were calculated through use of the extended Debye-Hückel equation. Although there are objections to the use of the Debye-Hückel equation in mixed electrolytes (16), it is apparent that the derived equilibrium constants are not greatly influenced by the method used to calculate activity coefficients. The values using the Debye-Hückel equation are included to permit direct comparison with other solubility data for calcium phosphates (17, 18, 19)

- (16) E. A. Guggenheim, "Thermodynamics", 3rd ed., North-Holland Publishing Co., Amsterdam, 1957, p. 355.
- (17) R. W. Mooney and G. J. Meisenhelter, J. Chem. Eng. Data 5, 373 (1960).
- (18) E. C. Moreno, W. E. Brown and G. Osborn, Soil Sci., Soc. Proc., 24, 94 (1960).
- (19) E. C. Moreno, T. M. Gregory and W. E. Brown, J. Res. NBS 72A (Phys. and Chem.) No. 6, 773 (1968).

Standard heats and entropies for the dissolution reaction for CaHPO_4 and the association reactions for CaHPO_4° and $\text{CaH}_2\text{PO}_4^+$ relate to their respective equilibrium constants by the linear function

$$\log K_i = -\frac{\Delta H_i^\circ}{2.303R} \left(\frac{1}{T}\right) + \frac{\Delta S_i^\circ}{2.303R} \quad (13)$$

The least squares results for each of the three reactions are given in Table IV. The data points in the plots of K_x and K_y vs $1/T$ were quite scattered, as indicated by the large errors in the derived quantities for the association reactions. These errors are much larger than the indicated errors in the same quantities for the dissolution reaction. This is attributed to the fact that the concentrations of the ion pairs were always small compared to the concentrations of unpaired ions.

DISCUSSION

Under the conditions used in these experiments, equilibrium was attained in a relatively short time, apparently because the solid phase was well crystallized and free of extraneous phases. Under these conditions, more basic calcium phosphates, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, $\beta\text{-Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ were not formed in significant amounts during the equilibration process even though under some of the conditions CaHPO_4 was metastable with respect to some of these salts. This is shown by the fact that essentially the same results were obtained whether equilibrium was attained (1) by leaching or by much longer batch equilibrations, or (2) by approaching equilibrium from supersaturated conditions.

The two values listed in the literature for the "apparent" solubility product of CaHPO_4 at 25° were calculated from the composition of solutions that had pH values much lower than those in this work. Elmore and Farr (5) calculated a K'_{sp} value for a single point (0.826% CaO and 2.387% P_2O_5) for which the pH was taken to be 2.80. Their value, 3.3×10^{-7} , would not differ greatly from the value one would get by extrapolating our data to this pH. The extrapolation cannot be done accurately because of the large curvature in the low pH region. The other value, 2.18×10^{-7} (2), was calculated from the invariant point composition for the solution in equilibrium with CaHPO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. This solution has a pH of about 1.01. Considering the uncertainties in the calculation and the difficulty of extrapolating our data to such a low pH, this value of K'_{sp} is reasonably close to ours.

The dependence of apparent solubility product constants on the pH of the equilibrated solution is consistent with the formation of the ion-pairs, CaHPO_4^0 and $\text{CaH}_2\text{PO}_4^+$. The fraction of calcium complexed, $\frac{\alpha}{M}$, shows the same trend with respect to pH as the apparent solubility products. Both have minima at the same pH. When corrections are made for ion-pair formation, "true" solubility product constants that are

independent of pH are obtained. This fact is shown by the small errors in the K_{sp} values listed in Table III.

The association constants, K_x and K_y , listed in Table III compare favorably with those obtained by other investigators using similar and different methods. Gergory, Moreno and Brown obtained the values $K_x = 479, 283, 264$, and 431 and $K_y = 9.7, 5.2, 3.7$, and 3.3 from solubility measurements on $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ at $5, 15, 25$, and 37°C , respectively (7), when the data was treated by the procedure outlined in this paper. Their values compare favorably with ours.

Chughtai, Marshall and Nancollas (18) determined association

(20) A. Chughtai, R. Marshall and G. H. Nancollas, J. Phys. Chem. 72, 208 (1968).

constants for CaHPO_4^0 and $\text{CaH}_2\text{PO}_4^+$ from potentiometric measurements on systems containing sodium, potassium and chloride ions in addition to those of the system $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$. Their values are $K_x(25^\circ\text{C}) = 5.48 \times 10^2$, $K_x(37^\circ\text{C}) = 6.81 \times 10^2$, $K_y(25^\circ\text{C}) = 25.6$ and $K_y(37^\circ\text{C}) = 31.9$; the values for K_y exceed ours by more than would be expected from our computed errors.

Davies and Hoyle (21) reported values of $K_x = 5 \times 10^2$

(21) C. W. Davies and B. E. Hoyle, J. Chem. Soc., 4134 (1953).

and $K_y = 11.8$ from a study of the effect of calcium ions on the pH of phosphate buffers at 25°C. These values are in reasonable agreement with ours.

The value for the standard heat of solution of CaHPO_4 reported in this work is about half the average value, $\Delta H = -9515$ calories per mole, calculated by Mooney and Meisenhelter (1) from the value of K'_{sp} given for 25°C by reference 2 and their solubility measurement at 90°C. The solubility constant at 90°C was based on a pH measured at 25°C. In view of the uncertainties in both solubility constant values and the large temperature range over which the calculation was made, great reliance cannot be given to this value of ΔH . A value of 9515 calories per mole would yield a much larger variation in solubility with temperature than would be consistent with our experimental errors.

Table I: Solubility and Ion-Pair Association Constants for Equilibria Approached from Undersaturation

M x 10 ⁴	Initial Composition of Saturated Solutions			$\frac{100c}{[M]}$	$10^7 K_{sp}^i$
	H_3PO_4	pH	Ca, M x 10 ⁴		
Leaching at 5 °C					
0.647 (-3) ^a	7.825 (-9) ^a	6.24 (+1)	6.93 (-4) ^a	7.7	2.28
5.20 (-8)	6.764 (-9)	9.16 (+3)	14.2 (+2)	5.6	2.18
10.1 (+1)	6.303 (+11)	13.4 (-1)	23.2 (+2)	4.4	2.07
47.2 (+2)	5.188 (+1)	49.3 (-5)	95.9 (+3)	3.9	2.09
92.5 (-3)	4.708 (-1)	93.0 (+2)	184. (+1)	5.4	2.12
286. (+1)	3.927 (+7)	279. (0)	560. (+4)	10.4	2.21
560. (-2)	3.509 (-5)	531. (-2)	1086. (+1)	15.3	2.47
Leaching at 15 °C					
1.95 (0)	7.189 (0)	6.33 (+2)	8.31 (+1)	5.1	1.79
5.08 (-1)	6.651 (+4)	8.49 (+4)	13.5 (+1)	4.3	1.72
10.1 (0)	6.212 (-8)	12.8 (-1)	22.9 (-1)	3.8	1.79
20.2 (+3)	5.692 (+4)	22.3 (-1)	43.0 (-3)	4.0	1.74
49.6 (+2)	5.041 (+1)	50.8 (0)	101. (0)	6.0	1.78
98.8 (-5)	4.564 (-3)	98.5 (-2)	196. (+1)	9.1	1.87
198. (-1)	4.094 (-2)	194. (0)	390. (+1)	13.7	1.98
494. (+1)	3.520 (+2)	466. (+1)	966. (-3)	22.4	
$K_{sp}^i = 1.97 \pm 0.03 \times 10^{-7}$					
$K_X = 2.43 \pm 0.32 \times 10^2$					
$K_Y = 5.2 \pm 0.7$					

Table I
(continued)

Initial H_3PO_4	Composition of Saturated Solutions				$\frac{100\alpha}{[M]}$	$10^7 K_{sp}$
	$M \times 10^4$	pH	$Ca, M \times 10^4$	$P, M \times 10^4$		
Leaching at 25° C						
1.03 (+2)	7.363 (+31) *	5.29 (-1)	6.29 (+5)	8.8	1.41	
4.85 (-2)	6.571 (-8)	7.97 (-7)	12.7 (0)	6.5	1.41	
9.98 (-12)	6.099 (-13)	12.2 (-2)	22.0 (0)	5.2	1.39	
24.6 (0)	5.420 (-4)	25.9 (+1)	51.0 (-4)	4.9	1.35	$K_{sp} = 1.25 \pm 0.02 \times 10^{-7}$
50.5 (-4)	4.901 (-8)	51.3 (-3)	101. (0)	6.4	1.40	$K_X = 3.65 \pm 0.55 \times 10^2$
99.5 (-2)	4.409 (+3)	99.3 (-5)	196. (+2)	9.4	1.40	$K_Y = 9.9 \pm 1.0$
100. (0)	4.405 (+6)	96.9 (+22) *	199. (0)	9.4	1.37	
201. (0)	3.940 (+4)	195. (+1)	398. (-1)	14.0	1.48	
502. (+4)	3.385 (-1)	472. (-9)	964. (+4)	22.5	1.73	
502. (+5)	3.381 (+1)	471. (-6)	972. (-1)	22.6	1.72	
Batch experiments at 25° C						
5.00 (-1)	6.560 (-5)	8.13 (-5)	13.1 (0)	4.9	1.44	
9.98 (-8)	6.095 (+1)	12.1 (+1)	22.0 (+1)	4.6	1.36	
47.4 (+1)	4.937 (+4)	48.5 (-1)	95.7 (+3)	5.0	1.37	$K_{sp} = 1.30 \pm 0.02 \times 10^{-7}$
99.5 (+1)	4.415 (0)	99.2 (-1)	199. (0)	7.4	1.43	$K_X = 3.36 \pm 0.53 \times 10^2$
99.5 (+1)	4.408 (+2)	102. (-2)	199. (+1)	7.4	1.44	$K_Y = 7.5 \pm 1.0$
201. (0)	3.948 (-3)	195. (0)	396. (0)	11.1	1.51	
201. (0)	3.945 (-1)	194. (+1)	399. (-3)	11.1	1.50	

(continued)

Initial H_3PO_4	Composition of Saturated Solutions				$\frac{100\alpha}{[M]}$	$10^7 K'_{SP}$
	$M \times 10^4$	pH	$Ca, M \times 10^4$	$P, M \times 10^4$		

Leaching at 37°C

5.12 (-8)	6.437 (-15)	7.30 (+1)	12.3 (0)	3.6	1.01
10.2 (+2)	5.896 (+23) *	11.9 (+1)	22.5 (-1)	3.2	0.93
10.5 (0)	5.912 (-2)	12.0 (+1)	22.8 (-2)	3.2	0.98
24.6 (+3)	5.274 (-4)	25.8 (0)	51.3 (-7)	3.8	1.00
51.1 (-6)	4.757 (+10)	50.1 (+7)	102. (-1)	5.7	1.01
52.1 (-1)	4.727 (-1)	53.0 (-8)	103. (+1)	5.8	0.99
102. (0)	4.248 (-5)	101. (+1)	207. (-2)	9.1	1.04
202. (+1)	3.790 (+9)	194. (0)	394. (+2)	13.7	1.05
202. (+1)	3.789 (+9)	194. (0)	397. (+1)	13.7	1.05
489. (+4)	3.271 (-4)	437. (-4)	932. (-6)	21.7	1.20

Batch experiments at 37°C

4.78 (+1)	6.450 (+2)	7.27 (+2)	12.1 (0)	6.3	1.01
23.6 (0)	5.307 (-1)	24.9 (-2)	48.3 (0)	4.3	0.98
97.9 (+7)	4.280 (-4)	98.7 (-12)	197. (-1)	8.0	1.05
199. (0)	3.808 (+5)	190. (+1)	389. (+1)	11.9	1.06
425. (-2)	3.370 (-2)	379. (+1)	804. (0)	17.6	1.20

* Numbers in parentheses are differences between experimental and adjusted values, see text.

^b K'_{SP} is the solubility product calculated disregarding ion-pair formation; K_{SP} , K_X and K_Y are defined by eq 1-3.

Table II: Solubility and Ion-Pair Association Constants for Equilibria Approached from Supersaturation

Composition of Solutions before and after leaching						$\frac{100\alpha}{[M]}$	$10^7 K_{SP}$	
pH	Ca, M $\times 10^4$			P, M $\times 10^4$			$\frac{100\alpha}{[M]}$	$10^7 K_{SP}$
	Before	After	Before	After	Before	After		
25°C								
6.753	6.554 (-5)	9.86	8.03 (-6)	14.7	13.1 (-2)	9.5	1.41	
6.707	6.515 (+11)	8.90	8.41 (-18)	15.0	13.0 (+3)	9.4	1.41	
5.139	4.894 (-4)	51.1	50.6 (0)	102.	101. (-1)	7.4	1.35	$K_{SP} = 1.20 \pm 0.04 \times 10^{-7}$
4.665	4.408 (-1)	99.3	98.7 (-3)	201.	197. (0)	10.4	1.39	$K_X = 5.92 \pm 1.67 \times 10^2$
4.115	3.957 (-4)	194.	193. (-2)	389.	387. (0)	15.2	1.50	$K_Y = 11.0 \pm 2.0$
3.603	3.392 (+5)	471.	453. (-1)	967.	939. (+5)	24.1	1.66	
37°C								
7.499	7.061 (+4)	7.66	5.03 (-8)	8.43	6.52 (+8)	8.6	1.04	
4.864	4.760 (-1)	49.3	49.1 (+5)	99.7	99.5 (-7)	6.0	0.98	$K_{SP} = 0.90 \pm 0.02 \times 10^{-7}$
4.826	4.725 (+2)	53.1	51.7 (+4)	106.	105. (-1)	6.2	1.08	$K_X = 4.58 \pm 1.13 \times 10^2$
4.362	4.227 (+1)	102.	102. (+1)	211.	210. (-2)	9.2	1.01	$K_Y = 9.5 \pm 1.7$
3.394	3.253 (0)	465.	448. (0)	964.	959. (0)	21.2	1.20	

Table III: Comparison of Solubility Products and Association Constants Derived Through Use of Davies and Debye-Hückel Equations for Activity Coefficients

t, °C	K _{sp} x 10 ⁷		K _x x 10 ²				K _y	
	Davies	Debye-Hückel	Davies	Debye-Hückel	Davies	Debye-Hückel	Davies	Debye-Hückel
5.00	1.97 ± 0.03	2.01 ± 0.03	2.43 ± 0.32	2.23 ± 0.30	5.2 ± 0.7	5.9 ± 0.7		
15.00	1.64 ± 0.01	1.66 ± 0.01	1.87 ± 0.24	1.73 ± 0.26	9.6 ± 0.6	10.8 ± 0.6		
25.00	1.25 ± 0.01	1.27 ± 0.01	3.77 ± 0.37	3.63 ± 0.36	9.6 ± 0.7	10.9 ± 0.7		
37.00	0.93 ± 0.01	0.94 ± 0.01	3.55 ± 0.62	3.19 ± 0.48	8.1 ± 0.6	9.7 ± 0.6		

Table IV: Thermodynamic Functions for CaHPO_4 , CaHPO_4° and $\text{CaH}_2\text{PO}_4^+$

Reaction	ΔH° kcal mol ⁻¹	ΔS° cal K ⁻¹ mol ⁻¹
$\text{CaHPO}_4(\text{s}) = \text{Ca}^{2+} + \text{HPO}_4^{2-}$	-4.17 ± 0.04 (-17.4 ± 0.2) ^a	-45.63 ± 0.41 (-190.9 ± 1.7) ^b
$\text{Ca}^{2+} + \text{HPO}_4^{2-} = \text{CaHPO}_4^\circ$	3.7 ± 1.1 (15.5 ± 4.6)	24 ± 4 (100 ± 17)
$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- = \text{CaH}_2\text{PO}_4^+$	1.2 ± 0.9 (5.0 ± 3.8)	8.2 ± 4.6 (34.3 ± 19.2)

^a values in kJ mol^{-1}

^b values in $\text{JK}^{-1} \text{ mol}^{-1}$

"1 cal = 4.184 J"

