cps) and CF–NF ($J_{CF^a-NF} = 24$ cps, $J_{CF^b-NF} = 13$ cps) coupling. The rather large magnitude of $J_{CF^a-CF^b}$ is not without precedent, for values as high as 270 cps have been observed for nonequivalent carbon fluorines adjacent to an asymmetric carbon[19] and, therefore, it is not unexpected in this case. In this ABX system the area ratio of the inner to outer doublets is 2.52:1 (theoretical 2.62:1).[20] Enhancement of the inner doublets is typical of spectra obtained when the chemical shift difference and spin–spin coupling values are similar; *i.e.*, for ClF_2CNFCl $\Delta\phi_{CF^a-CF^b}$ (cps)/$J_{CF^a-CF^b}$ (cps) $\cong 2$. CF^a is centered at ϕ 55.6 and CF^b at ϕ 52.9 while the broad unresolved NF fluorine is found at ϕ −7.2. An integration of the total spectrum gives NF = 1.0 and $CF^a = CF^b = 0.98$.

An attempt to collapse the two CF multiplets proved unsuccessful. At −60° the centers of the two CF multiplets are separated by 330 cps but are shifted to about 237 cps at +60°. At 100° the peaks still do not coalesce. Higher temperatures were not attempted due to excessive pressure from the ClF_2CNFCl–CCl_3F mixture in the nmr tube.

An interesting aspect of the temperature study of the magnetically nonequivalent nuclei in $(CF_3)_2FCNFCl$ and ClF_2CNFCl is the rather high temperature of coalescence, especially for the latter compound in which the CF resonances are separated by 237 cps at 60°. Other workers have found that when highly electronegative substituents, particularly halogens, are bonded to the asymmetric nitrogen, there is a significant rise in the temperature of coalescence.[6,21,22] The collapse of the CF_3 groups in $(CF_3)_2FCNFCl$ at 60° can be rationalized in terms of the relatively bulky CF_3 groups which would increase the inversion rate because of greater steric interactions when the substituents are in a pyramidal position.[23]

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Solubility Study of Calcium Hydrogen Phosphate. Ion-Pair Formation[1a]

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The solubility of $CaHPO_4$ has been determined in the ternary system $Ca(OH)_2$–H_3PO_4–H_2O, at 5, 15, 25, and 37°. The solubility product constant, $K_{sp} = (Ca^{2+})(HPO_4^{2-})$, varies with pH unless formation of ion pairs $CaHPO_4^0$ and $CaH_2PO_4^+$ is taken into consideration. Solubility product constants and their standard errors for $CaHPO_4$ are $(1.97 \pm 0.03) \times 10^{-7}$, $(1.64 \pm 0.01) \times 10^{-7}$, $(1.26 \pm 0.02) \times 10^{-7}$, and $(0.92 \pm 0.02) \times 10^{-7}$ at 5, 15, 25, and 37°, respectively. Association constants and standard errors are $(2.4 \pm 0.3) \times 10^2$, $(1.9 \pm 0.2) \times 10^2$, $(3.8 \pm 0.5) \times 10^2$, and $(3.9 \pm 0.9) \times 10^2$ for $CaHPO_4^0$ and 5 ± 1, 10 ± 1, 10 ± 1, and 11 ± 1 for $CaH_2PO_4^+$ at the same respective temperatures. Thermodynamic functions for the dissolution reaction for $CaHPO_4$ and the association reactions for $CaHPO_4^0$ and $CaH_2PO_4^+$ are also presented.

Introduction

Anhydrous calcium hydrogen phosphate, $CaHPO_4$, is a stable phase in the system $Ca(OH)_2$–H_3PO_4–H_2O. 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°,[2,3] but these are not 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 relatively high concentrations 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 $CaHPO_4^0$ and $CaH_2PO_4^+$ are reported for 5, 15, 25, and 37°. Equilibrations were made in the ternary system to avoid complications in the interpretation of data which might result from the presence of other ions.

[1] (a) This paper is based on a dissertation submitted by Hershel McDowell to the faculty of Howard University in partial fulfillment of the requirement for the Ph.D. degree. (b) Director, Research Associate Program of the American Dental Association at the National Bureau of Standards. (c) To whom reprint requests should be made at Howard University.

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Experimental Section

Chemicals.—The $CaHPO_4$ was prepared by dehydration of $CaHPO_4 \cdot 2H_2O$. The $CaHPO_4 \cdot 2H_2O$ was prepared in pure, well-crystallized form by ammoniating an aqueous solution, initially saturated with $Ca(H_2PO_4)_2 \cdot H_2O$, in an ice bath. The dehydration was accomplished by boiling 400 g of $CaHPO_4 \cdot 2H_2O$ in 4 l. of 0.07 M phosphoric acid for 72 hr. After the reaction was complete, the resulting $CaHPO_4$ was collected by filtration and washed with small volumes of distilled water until the pH of the wash solution reached 6.0. The $CaHPO_4$ was then washed thoroughly with acetone and dried *in vacuo* (3 hr at 80°, then 60 hr at 50°). 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 $CaHPO_4 \cdot 2H_2O$ crystals had converted into multicrystalline $CaHPO_4$ with an average domain size of about 20 μm. *Anal.* Calcd for $CaHPO_4$: Ca, 29.46; P, 22.71. Found: Ca, 29.49 ± 0.10; P, 22.71 ± 0.06.

Doubly crystallized phosphoric acid hemihydrate, $2H_3PO_4 \cdot H_2O$, 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 molybdovanadate reagent of Brabson, *et al.*[5] 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 ±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 ±1.5% of the calcium in the sample. The pH measurements were made with a Beckman Research pH meter, Model 101900,[6] 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 unit.

Equilibrations.—Leaching experiments were performed at 5, 15, 25, and 37° in which a dilute phosphoric acid solution was passed through a column of $CaHPO_4$. "Batch experiments" (in which $CaHPO_4$ was rotated with dilute phosphoric acid) and "supersaturation experiments" (in which a solution supersaturated with respect to $CaHPO_4$ was passed through a column of the salt) were performed only at 25 and 37°. The batch and supersaturation experiments were used to confirm that equilibrium had been established in the leaching process. Two temperatures were considered sufficient for this purpose.

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 ±0.01°. 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 and replicate samples of these were analyzed for calcium and for phosphorus.

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 7 days, it was shown that equilibrium was attained within 24 hr. Thereafter, solutions equilibrated for about 24 hr 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 $CaHPO_4 \cdot 2H_2O$ at room temperature or a column of $CaHPO_4$ at a temperature 10° 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[7] 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_{sp}, allowance was made for ion-pair formation. The equilibria, in addition to those for the dissociation constants of phosphoric acid, are defined by the equations

$$CaHPO_4(s) = Ca^{2+} + HPO_4^{2-}, \quad K_{sp} = (Ca^{2+})(HPO_4^{2-}) \tag{1}$$

$$Ca^{2+} + HPO_4^{2-} = CaHPO_4^0, \quad K_x = \frac{(CaHPO_4^0)}{(Ca^{2+})(HPO_4^{2-})} \tag{2}$$

$$Ca^{2+} + H_2PO_4^- = CaH_2PO_4^+, \quad K_y = \frac{(CaH_2PO_4^+)}{(Ca^{2+})(H_2PO_4^-)} \tag{3}$$

The relationships between the solubility product K_{sp} 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. In order to solve the above equations for K_{sp}, K_x,

$$K_x = \frac{(CaHPO_4^0)}{K_{sp}} \tag{4}$$

$$K_y = \frac{K_2(CaH_2PO_4^+)}{K_{sp}(H^+)} \tag{5}$$

and K_y, approximate values for these constants were chosen. These values were improved by a least-squares adjustment procedure[8a] based on the method of Deming,[8b] which 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

$$2[Ca^{2+}] + [H^+] + [CaH_2PO_4^+] - [OH^-] - [H_2PO_4^-] - 2[HPO_4^{2-}] - 3[PO_4^{3-}] = 0 \tag{6}$$

$$[M - \alpha][P - \alpha]\frac{f_{Ca}}{\lambda} - K_{sp} = 0 \tag{7}$$

$$\frac{[M]}{[P - P_0]} - 1 = 0 \tag{8}$$

where[4]

$$\lambda = \frac{(H^+)^2}{K_1K_2} + \frac{(H^+)}{K_2f_1} + \frac{1}{f_2} + \frac{K_3}{(H^+)f_3} \tag{9}$$

K_1,[9] K_2,[10] and K_3[11] are the first, second, and third dissociation constants of phosphoric acid; f_{Ca} f_1, f_2, and f_3 are the activity coefficients of Ca^{2+}, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}, respectively;

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TABLE I

SOLUBILITY AND ION-PAIR ASSOCIATION CONSTANTS FOR EQUILIBRIA APPROACHED FROM UNDERSATURATION

Initial	Composition of saturated solutions					
$[H_3PO_4] \times 10^4$, *M*	pH	10^4[Ca], *M*	10^4[P], *M*	$100\alpha/M$	$10^7K_{sp}'^{b}$	
Leaching at 5°						
0.647 (−3)[a]	7.825 (−9)[a]	6.24 (+1)[a]	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	$K_{sp}^{b} = (1.97 \pm 0.03) \times 10^{-7}$
47.2 (+2)	5.188 (+1)	49.3 (−5)	95.9 (+3)	3.9	2.09	$K_x = (2.4 \pm 0.3) \times 10^2$
92.5 (−3)	4.708 (−1)	93.0 (+2)	184 (+1)	5.4	2.12	$K_y = 5.2 \pm 0.7$
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°						
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	$K_{sp} = (1.64 \pm 0.01) \times 10^{-7}$
20.2 (+3)	5.692 (+4)	22.3 (−1)	43.0 (−3)	4.0	1.74	$K_x = (1.9 \pm 0.2) \times 10^2$
49.6 (+2)	5.041 (+1)	50.8 (0)	101 (0)	6.0	1.78	$K_y = 9.6 \pm 0.6$
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		
Leaching at 25°						
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	
50.5 (−4)	4.901 (−8)	51.3 (−3)	101 (0)	6.4	1.40	$K_{sp} = (1.25 \pm 0.02) \times 10^{-7}$
99.5 (−2)	4.409 (+3)	99.3 (−5)	196 (+2)	9.4	1.40	$K_x = (3.7 \pm 0.6) \times 10^2$
100 (0)	4.405 (+6)	96.9 (+22)*	199 (0)	9.4	1.37	$K_y = 9.9 \pm 1.0$
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)	3.382 (+1)	471 (−6)	972 (−1)	22.6	1.72	
Batch Experiments at 25°						
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	$K_x = (3.4 \pm 0.5) \times 10^2$
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	
Leaching at 37°						
5.12 (−7)	6.437 (−17)	7.30 (+7)	12.3 (+1)	5.0	1.01	
10.1 (+1)	5.951 (−17)	12.0 (−1)	22.3 (−3)	4.6	1.00	
10.2 (+1)	5.896 (+29)	11.9 (+1)	22.5 (−2)	4.6	0.93	
10.5 (0)	5.912 (−1)	12.0 (+1)	22.8 (−2)	4.6	0.98	
24.6 (+3)	5.274 (−3)	25.8 (0)	51.3 (−4)	5.8	1.00	
51.1 (−4)	4.757 (−11)	50.1 (+9)	102 (0)	8.8	1.01	$K_{sp} = (0.93 \pm 0.02) \times 10^{-7}$
52.1 (−1)	4.727 (+1)	53.0 (−1)	103 (+1)	8.9	0.99	$K_x = (3.1 \pm 0.9) \times 10^2$
102 (+1)	4.248 (−6)	101 (+1)	207 (−1)	13.8	1.04	$K_y = 14.6 \pm 1.5$
104 (+1)	4.227 (+8)	102 (+1)	210 (−2)	13.9	1.04	
202 (0)	3.790 (+9)	194 (−1)	394 (+2)	20.7	1.05	
202 (+1)	3.789 (+10)	194 (0)	397 (0)	20.7	1.05	
489 (+3)	3.271 (−5)	437 (−2)	932 (−7)	32.6	1.20	
Batch Experiments at 37°						
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	$K_{sp} = (0.93 \pm 0.01) \times 10^{-7}$
97.9 (+7)	4.280 (−4)	98.7 (−12)	197 (−1)	8.0	1.05	$K_x = (4.6 \pm 0.6) \times 10^2$
199 (0)	3.808 (+5)	190 (+1)	389 (+1)	11.9	1.06	$K_y = 8.4 \pm 0.7$
425 (−2)	3.370 (−2)	379 (+1)	804 (0)	17.6	1.20	

[a] 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.

and α, the total concentration of ion pairs in a given solution, is given by

$$\alpha = {}^1/_2[M + P] - {}^1/_2\{[M + P]^2 - 4[MP - \lambda K_{sp}/f_{Ca}]\}^{1/2} \qquad (10)$$

where M and P are the total calcium and phosphorus concentrations and P_0 is the analytical concentration of the initial phosphoric acid. In these equations, parentheses indicate molar activities and brackets indicate molar concentrations. Ionic strengths were calculated from the equation

$$I = {}^1/_2\Sigma C_i z_i^2 \qquad (11)$$

where C_i is the concentration of the ith ion and z_i is its charge. Activity coefficients were calculated using the equation[6]

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

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°, respectively.[12] The activity coefficient for $CaH_2PO_4^+$ was assumed

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TABLE II
SOLUBILITY AND ION-PAIR ASSOCIATION CONSTANTS FOR EQUILIBRIA APPROACHED FROM SUPERSATURATION

Composition of solutions before and after leaching								
pH		10^4[Ca], M		10^4[P], *M*				
Before	After	Before	After	Before	After	$100\alpha/M$	$10^7K_{sp}'$	
25°								
6.753	6.554 (−5)	9.86	8.03 (−6)	14.7	13.1 (−2)	9.5	1.41	$K_{sp} = (1.20 \pm 0.04) \times 10^{-7}$ $K_x = (5.9 \pm 1.7) \times 10^2$ $K_y = 11 \pm 2$
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	
4.665	4.408 (−1)	99.3	98.7 (−3)	201	197 (0)	10.4	1.39	
4.115	3.957 (−4)	194	193 (−2)	389	387 (0)	15.2	1.50	
3.603	3.392 (+5)	471	453 (−1)	967	939 (+5)	24.1	1.66	
37°								
7.499	7.061 (+4)	7.66	5.03 (−8)	8.43	6.52 (+8)	8.6	1.04	$K_{sp} = (0.90 \pm 0.02) \times 10^{-7}$ $K_x = (4.6 \pm 1.1) \times 10^2$ $K_y = 9.5 \pm 1.7$
4.864	4.760 (−1)	49.3	49.1 (+5)	99.7	99.5 (−7)	6.0	0.98	
4.826	4.725 (+2)	53.1	51.7 (+4)	106	105 (−1)	6.2	1.08	
4.362	4.227 (+1)	102	102 (+1)	211	210 (−2)	9.2	1.01	
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

	10^7K_{sp}		10^2K_x		K_y	
Temp, °C	Davies	Debye–Hückel	Davies	Debye–Hückel	Davies	Debye–Hückel
5.00	1.97 ± 0.03	2.01 ± 0.03	2.4 ± 0.3	2.2 ± 0.3	5 ± 1	6 ± 1
15.00	1.64 ± 0.01	1.66 ± 0.01	1.9 ± 0.2	1.7 ± 0.3	10 ± 1	11 ± 1
25.00	1.26 ± 0.02	1.27 ± 0.02	3.8 ± 0.4	3.6 ± 0.4	10 ± 1	11 ± 1
37.00	0.92 ± 0.02	0.93 ± 0.02	3.9 ± 0.9	3.6 ± 0.7	11 ± 1	12 ± 1

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]

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 per cent 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 eq 1–3, 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[14] on $(gN - b)$ degrees of freedom, where g 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 derived constants in Table II are in reasonable agreement with the corresponding values in Table I (when proper allowance is given for the calculated errors), we assume that the precipitate in the equilibrations from supersaturation was $CaHPO_4$ and not $CaHPO_4 \cdot 2H_2O$. This was confirmed by a plot of the chemical potential of $Ca(OH)_2$ against that of H_3PO_4[15] which revealed that 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 overall mean value. The greatest deviation in the derived constants is that for K_x obtained from supersaturation at 25°. When this value is excluded in calculating the weighted mean, a value of $K_x = (3.6 \pm 0.5) \times 10^2$ is obtained which deviates insignificantly from the value $(3.8 \pm 0.4) \times 10^2$ obtained when it is included. 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 con-

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[13] Provided by E. C. Moreno and T. M. Gregory.

[14] N. Arley and K. R. Buch, "Introduction to the Theory of Probability and Statistics," Wiley, New York, N. Y., 1950, Chapter 12.

[15] (a) E. C. Moreno, W. L. Lindsay, and G. Osborn, *Soil Sci.*, **90**, 59 (1960); (b) K. MacGregor and W. E. Brown, *Nature (London)*, **205**, 359 (1965).

[16] E. A. Guggenheim, "Thermodynamics," 3rd ed, North-Holland Publishing Co., Amsterdam, 1957, p 355.

stants are not greatly influenced by the method used to calculate activity coefficients. The values obtained using the Debye–Hückel equation are included to permit direct comparison with other solubility data for calcium phosphates.[17–19]

Standard heats and entropies for the dissolution reaction for $CaHPO_4$ and the association reactions for $CaHPO_4^0$ and $CaH_2PO_4^+$ were calculated from the van't Hoff expression over the temperature range 5–37°. The least-squares results for each of the three reactions are given in Table IV. The data points in the plots of log K_x and log K_y *vs.* $1/T$ were quite scattered, as indicated by the large errors in the derived quantities for the association reactions. These errors[20] 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.

TABLE IV
THERMODYNAMIC FUNCTIONS FOR $CaHPO_4$, $CaHPO_4^0$, AND $CaH_2PO_4^+$

Reaction	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal deg^{-1} mol^{-1}
$CaHPO_4(s) = Ca^{2+} + HPO_4^{2-}$	-4.1 ± 0.3	-45.4 ± 0.1
	$(-17.2 \pm 1.3)^a$	$(190 \pm 1)^b$
$Ca^{2+} + HPO_4^{2-} = CaHPO_4^0$	3.3 ± 1.9	23 ± 7
	(14 ± 8)	(96 ± 29)
$Ca^{2+} + H_2PO_4^- = CaH_2PO_4^+$	3.6 ± 1.5	16 ± 5
	(15 ± 6)	(67 ± 21)

[a] Values in kJ mol^{-1}. [b] Values in J deg^{-1} mol^{-1} (1 cal = 4.184 J).

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, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, β-$Ca_3(PO_4)_2$, and $Ca_{10}(PO_4)_6(OH)_2$, 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[3] calculated a K_{sp}' value for a single point (0.826% CaO and 2.38% 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 $Ca(H_2PO_4)_2 \cdot H_2O$. 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.

It should be noted, also, that Farr[2] gave the value 2.18×10^{-7} for the solubility constants for both of the salts $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$. Van Wazer[21] justified that they should have the same solubility constants on the basis that "the activity of water at the invariant point where $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ are in equilibrium" is very nearly 1. Actually, the two salts cannot be in equilibrium with one another (*i.e.*, do not have an invariant point) except under specific conditions of temperature and pressure. A comparison of our data with those of Gregory, *et al.*,[7] indicates that at atmospheric pressure the temperature at which the two salts can be in coequilibrium must be below 5°. Under standard conditions, the reaction $CaHPO_4(c) + 2H_2O(l) \rightarrow CaHPO_4 \cdot 2H_2O(c)$ is accompanied by a 11% decrease in volume. Higher pressures, therefore, will increase the stability of $CaHPO_4 \cdot 2H_2O$ (and, therefore decrease its solubility product) relative to that of $CaHPO_4$.

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 $CaH_2PO_4^+$. The fraction of calcium complexed, α/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. Gregory, 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 $CaHPO_4 \cdot 2H_2O$ at 5, 15, 25, and 37°, respectively,[8a] when the data were treated by the procedure outlined in this paper. Their values compare favorably with ours.

Chughtai, Marshall, and Nancollas[22] determined association constants for $CaHPO_4^0$ and $CaH_2PO_4^+$ from potentiometric measurements on systems containing sodium, potassium, and chloride ions in addition to those of the system $Ca(OH)_2$–H_3PO_4–H_2O. Their values are $K_x(25°) = 5.48 \times 10^2$, $K_x(37°) = 6.81 \times 10^2$, $K_y(25°) = 25.6$, and $K_y(37°) = 31.9$; the values for K_y exceed ours by more than would be expected from our computed errors.

Davies and Hoyle[23] reported values of $K_x = 5 \times 10^2$ and $K_y = 11.8$ from a study of the effect of calcium ions on the pH of phosphate buffers at 25°. These values are in reasonable agreement with ours.

In a very recent paper, Childs[24] has reported results of a potentiometric titration of a solution containing 0.008 *M* Ca, 0.008 *M* H_3PO_4, and 0.15 *M* KNO_3 with KOH at 37°. He reported values for $K_x = 20 \pm 2$ and $K_y = 4 \pm 2$. However, these values were obtained

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(18) E. C. Moreno, W. E. Brown, and G. Osborn, *Soil Sci. Soc. Amer., Proc.*, **24**, 94 (1960).

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using a model containing the species $H_5(PO_4)_2^-$, $H_4(PO_4)_2^{2-}$, $H_3(PO_4)_2^{3-}$, $CaH_3(PO_4)_2^-$, and $Ca_2H_2(PO_4)_2^0$ in addition to those used here. Childs' values for K_x and K_y are both smaller than those reported here as well as others discussed above. This is consistent with the use of more species in his model. It was not necessary for us to assume these additional species in order to obtain constancy in the K_{sp} for $CaHPO_4$. Precipitation might account for the apparent presence of the other calcium phosphate ion associations given by Childs. A calculation of ion activity products for the solutions of higher pH given by Childs in his Table VI shows that these solutions were supersaturated with respect to the solids $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $Ca_2H_8(PO_4)_6 \cdot 5H_2O$, β-$Ca_3(PO_4)_2$, and $Ca_5(PO_4)_3OH$. One or more of these may have formed as a colloidal precipitate which was not detected.

The value for the standard heat of solution of $CaHPO_4$ reported in this work is about half the average value, $\Delta H = -9515$ cal mol^{-1}, calculated by Mooney and Meisenhelter[17] from the value of K_{sp}' given for 25° by ref 2 and their solubility measurement at 90°. The solubility constant at 90° was based on a pH measured at 25°. 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 cal mol^{-1} would yield a much larger variation in solubility with temperature than would be consistent with our experimental errors.

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Phosphonitrilic Compounds. X.[1] Synthesis of Spirophosphazenes with Five-, Six-, and Seven-Membered Exocyclic Rings at Phosphorus

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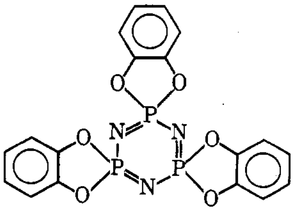
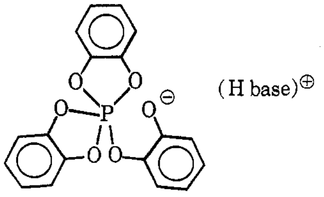
Spirocyclophosphazenes are formed when 1,8-dihydroxynaphthalene and a base react with $(NPCl_2)_{3 \text{ or } 4}$ or when 2,2′-dihydroxybiphenyl and base react with $(NPCl_2)_4$. However, catechol (1,2-dihydroxybenzene) and base interact with $(NPCl_2)_4$ to yield a phosphorane (II), rather than the spirophosphazene formed with $(NPCl_2)_3$. These differences are ascribed to the effects of ring strain when five-membered exocyclic rings are present.

Introduction

In an earlier paper[2] we reported the synthesis of tris(*o*-phenylenedioxy)cyclotriphosphazene (I) by the interaction of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with catechol in the presence of triethylamine or pyridine as hydrohalide acceptors.



I



II

A number of other spirocyclic trimers analogous to I have also been prepared in which the side units were 2,3-dioxynaphthyl, 2,2′-dioxybiphenyl, toluene-3,4-dithio, or *o*-phenylenediamino.[3] Aliphatic spiro derivatives have also been described.[4,5] During our earlier work we encountered difficulty with the preparation of spirocyclic cyclotetraphosphazenes derived from octachlorocyclotetraphosphazene, $(NPCl_2)_4$. Thus, the interaction of $(NPCl_2)_4$ with catechol and triethylamine yielded a phosphorane (II) rather than a spirophosphazene.[2] Similar results were observed with high polymeric $(NPCl_2)_n$.[2] This behavior was in marked contrast to the brief report by other investigators[5,6] that the tetrameric analog of I could be prepared from $(NPCl_2)_4$ and catechol in pyridine solution, a result that we have so far been unable to repeat. It was of some interest, therefore, to attempt the synthesis of cyclotetraphosphazenes with five-, six-, and seven-membered exocyclic dioxyaryl side groups and to ascertain the influence of exocyclic ring size on the ease of cyclization.

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