

Rates of Solution of Calcium Phosphates In Phosphoric Acid Solutions

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Information about the complex chemistry of phosphate in soil systems was obtained from measurements of the rates of solution of eight synthetic calcium phosphates and three natural fluorapatites in dilute solutions of phosphoric acid. The rates of solution vary inversely with the pH of the solvent. The effects of temperature and stirring show that the rates for the calcium orthophosphates are controlled by diffusion, and approximate diffusion coefficients are presented. The rate for vitreous calcium metaphosphate is controlled by chemical reaction, probably hydrolytic degradation.

SOIL SYSTEMS are complex and heterogeneous mixtures of many components. The presence of growing plants in such a system, and their withdrawal of components from the system, add to the complexity. The processes that take over upon introduction of a phosphorus fertilizer into a soil-plant system are poorly understood. The work described here is directed toward a better understanding of these processes.

Phosphorus fertilizers usually are added to the soil as solids, but to be utilized by plants, the phosphorus must first dissolve. The solubility of most calcium phosphates in water (22) is as high as the minimal phosphorus concentration required for normal growth of vegetation in solution culture (33), but equilibrium solubility may never be attained in a dynamic system. In a consideration of the solute phosphorus concentration in soils and the uptake of phosphorus by a crop, Pierre (34) has emphasized the importance of the rate of dissolution of phosphates in the utilization of fertilizer phosphorus by plants.

McGeorge (28) correlated plant response with the rate of removal of phosphate from soils by electro dialysis. The kinetics of the dissolution of apatites in concentrated acids (4, 8) and in solutions saturated with calcium phosphates (26) have been investigated in connection with the manufacture of fertilizers.

The hydrogen ion activity of the solvent undoubtedly is a major governing factor in the rates of solution of calcium phosphates. With the exception of a few preliminary measurements, phosphoric acid was the only solvent in the present work. Through adherence to the one acid, the possible complicating effect of nonphosphorus anion species was avoided and a special interest in reactions in phosphoric acid

was served. The rates of solution of eight synthetic calcium phosphates and three natural fluorapatites were measured.

Materials

The more basic synthetic phosphates (fluorapatite, hydroxyapatite, and tricalcium phosphate) were prepared by thermal methods, because these methods yield well-characterized compounds. Although these preparations may dissolve at rates different from those of basic phosphates freshly precipitated in soils, the possible difference was accepted in preference to the alternative of working with ill-defined materials. Significance could be attached at least to the relative rates of solution of the well-characterized preparations.

Monocalcium phosphate monohydrate and anhydrous dicalcium phosphate (27), β -tricalcium phosphate, and fluorapatite (12), and vitreous calcium metaphosphate (17, 20) were prepared by other methods. Large crystals (1 by 2 by 0.5 cm.) of dicalcium phosphate dihydrate were grown by interdiffusion of aqueous solutions of ammonium phosphate and calcium nitrate at room temperature. An outer jar held an aqueous solution of monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), 100 grams per liter, pH 3. An inner jar held an aqueous solution of calcium nitrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$],

100 grams per liter, pH 3 (adjusted with nitric acid). The salts diffused through a superimposed layer of nitric acid at pH 3.

Potassium calcium pyrophosphate ($\text{K}_2\text{CaP}_2\text{O}_7$), an experimental fertilizer, was prepared by heating, at 1200°C ., a mixture of mono- and tripotassium phosphates and anhydrous dicalcium phosphate in which the mole ratio calcium oxide-potassium oxide-phosphorus pentoxide was 4:5:5. The cooled product was a mixture of crystals of potassium calcium pyrophosphate and a potassium phosphate glass. The glass was extracted with hot water, leaving the crystals of pyrophosphate.

Hydroxyapatite was prepared by heating a mixture of monocalcium phosphate monohydrate and calcium carbonate in an atmosphere of water vapor at 1200°C . The product was ground and extracted with neutral ammonium citrate solution to remove nonapatite phosphates.

The synthetic phosphates were of relatively high purity. Their x-ray and optical properties agreed with the published values (such values for potassium calcium pyrophosphate have not been published). The β -tricalcium phosphate, however, contained 0.6% of pyrophosphate. The anhydrous dicalcium phosphate contained about 0.1% of nonorthophosphate and 0.4% excess phosphoric oxide. The vitreous cal-

Table I. Composition of Natural Fluorapatites

Source	Composition, %				Impurities Detected
	CaO	P ₂ O ₅	F	CO ₂	
South America	55.8	40.4	3.3	0.4	Cl, Ag, Al, Ce, Fe, La, Mg, Mn, Na, Pb, Si, Sr, Yb, Y
Mexico	55.6	41.3	3.3	0.1	Cl, Ag, Al, Ce, Fe, La, Mg, Mn, Na, Pb, Si, Sr, Yb, Y
Canada	54.3	40.0	3.4	0.3	Cl, Fe, Mg, Mn, Na, Si, Sr
Ca ₁₀ (PO ₄) ₆ F ₂	55.6	42.2	3.77	(theoretical)	

cium metaphosphate was about 0.2% low in phosphoric oxide. The compositions of the natural fluorapatites are shown in Table I.

The solvent phosphoric acid solutions were prepared from conductance water and triply crystallized orthophosphoric acid or its hemihydrate. The compositions of the phosphoric acid solutions were determined from their conductivity (29) and density (9). The relationship between acid molality and pH is shown in columns 2 and 3 of Table VII.

Surface Area and Character

In heterogeneous reactions, surface area is a very important quantity, the rate of the process being proportional to the amount of "effective" surface. When the rate is controlled by diffusion in an interfacial liquid layer, microscopic surface roughness and fine porosity are not important, because the solid is masked by the thin surrounding liquid layer. The apparent surface of the liquid layer is approximately the effective area. When the rate is controlled by the chemical reaction between the solid and liquid, microscopic roughness and porosity are important, thus the effective surface differs from that for a diffusion-controlled reaction.

The materials under study varied considerably in their surface characteristics. All the synthetic calcium orthophosphates, except monocalcium phosphate monohydrate and dicalcium phosphate dihydrate, were very fine crystals. The forms of these crystals varied greatly.

After the anhydrous dicalcium phosphate was ground and screened through a 200-mesh sieve, it was further sized by elutriation, and a sample of essentially uniform particle size was obtained. The sample consisted of single crystals and rosette aggregates of fine crystals. Upon partial dissolution, all the particles were pitted, and the aggregates began to disintegrate at about 70% dissolution.

The synthetic apatites were ground and screened through a 325-mesh screen. The fluorapatite particles were of relatively uniform size and shape. Many of the particles were agglomerates which began to disintegrate when about 30% of a sample was dissolved. The hydroxyapatite was composed of two types of particles—plate crystals and round aggregates of fine crystals. These aggregates disintegrated over the entire range of dissolution.

The minus 200-mesh potassium calcium pyrophosphate was composed of relatively uniform crystals that dissolved without developing erratic shape.

The β -tricalcium phosphate was the least satisfactory material with regard to surface. The minus 200-mesh material was composed of loosely knit,

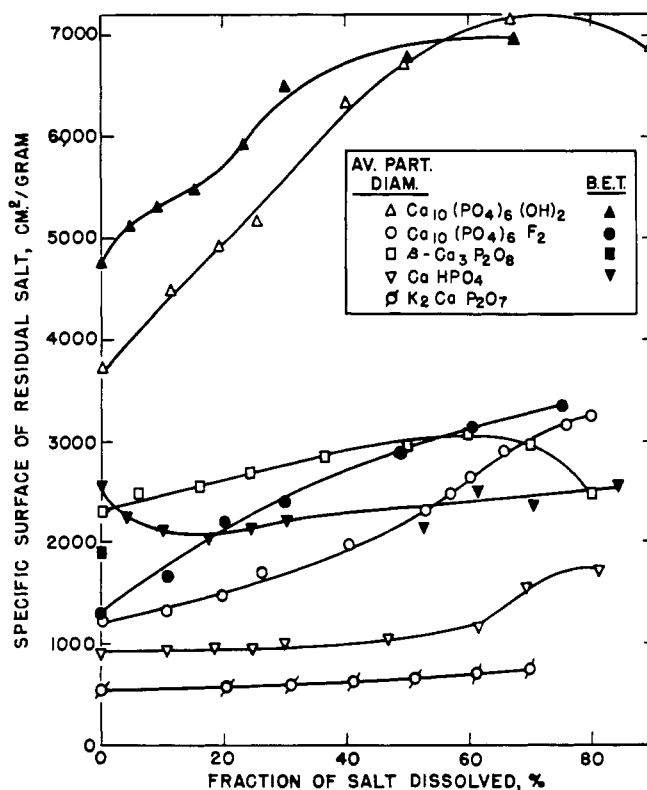


Figure 1. Change in specific surface of calcium phosphates with dissolution

chainlike aggregates of fine crystals, varying greatly in shape and size and in their tendency to disintegrate. These properties magnified the uncertainty in the effective surface.

In many of the experiments, the amount of effective surface changed markedly during dissolution. The powdered materials were so varied in particle shape and size, especially as dissolution progressed, as to make impractical the calculation of their surfaces at different degrees of dissolution by use of shape factors. To follow the change of specific surface accompanying dissolution of the powdered samples, surface areas were measured after different fractions of the salts had been dissolved. The specific surface of the anhydrous dicalcium phosphate, hydroxyapatite, and fluorapatite were measured by a low temperature gas-adsorption method (2). Surface areas of all the powdered samples were calculated from the average particle diameters as measured by an air-permeability method (76). Plots of the change in specific surface with increasing dissolution are shown in Figure 1. The areas calculated from average particle diameters are the ones used in rate calculations, because they are believed to approximate more closely the effective areas for the process that was found to be rate-controlling in these experiments.

The dimensions of the macrocrystalline monocalcium phosphate monohydrate were measured under a low-power

microscope, and the specific surface of the sample was calculated from averages of the measurements. Surface areas of the macrocrystals of dicalcium phosphate dihydrate, and of the cylinders that were cut from natural fluorapatite and vitreous calcium metaphosphate, were calculated from micrometer measurements of the specimens. The cylinders were from 1 to 2 cm. in diameter and 1.8 to 2.5 cm. long.

Rate Measurements

Hydroxy- and fluorapatite dissolved at the same rate in a phosphoric acid solution with a pH above 1 as in a hydrochloric acid solution with the same pH; therefore, phosphoric acid solutions were adopted as solvents to avoid the complications that might result from the addition of the extraneous chloride ion to the system. The initial pH of the solvents ranged from 0.48 to 4 and the final pH was as high as 6.

Because of the great differences in the rates at different pH's, it was necessary to use several methods of measurement to cover the range of pH. The progress of the dissolution process was followed through measurement of the associated heat effect, the change in electrical conductance of the solution, or the loss of weight by the specimen of solid.

An attempt to measure the rate of solution of radioactive fluorapatite (73) in water was unsuccessful. The container was coated with butyl methacry-

late to minimize the adsorption of phosphate (17); however, as much as 40% of the dissolved phosphate, at concentrations up to 0.1 p.p.m., was adsorbed on the surface of the apparatus. Methods simpler than tracer methods served for the measurements in acid solutions.

Calorimetric Method. The calorimetric method was based on the rate of evolution of heat upon dissolution of a salt in a solvent acid in a modification of the Southard solution colorimeter (36). The resistance thermometer was an unbalanced bridge composed of two opposite arms of manganin resistors, and two thermistors (Western Electric Co., No. 14B). Different thermometers were used for measurements at 15° and 25° C. The temperature coefficient or resistance of the thermistors was approximately -5% per 1° C. and the bridge current was 1.00 ma. The bridge current and the potential drop across standard resistors were measured with precision potentiometers and galvanometers. The heater for calibrating the calorimeter was a 40-ohm Calrod element mounted on the frame that supported the thermistors. The thermometer frame was made of 1/8-inch thin-walled Inconel tubing. The thermometer and its mount had a low heat capacity and the response to small changes in temperature was rapid.

The change in temperature of the solution was reflected in a voltage drop across the thermometer, which was recorded continuously by a Leeds & Northrup Speedomax. The recorder chart could be read to 0.02 mv., which corresponded to 0.0005° C. and 0.58 cal. for the 25° C. thermometer, and to 0.0003° C. and 0.38 cal. for the 15° C. thermometer.

The calorimetric rate measurements were designed to minimize change in the pH of the solvent during an experiment. From 600 to 1200 grams of solvent and from 0.25 to 10 grams of salt were used in a measurement. The pH of the solvent acids ranged from 1 to 3.1.

After the heat of stirring was determined, the calcium phosphate was added to the acid and the rate of evolution of heat upon dissolution was measured. The calorimeter constant then was determined and the final heat of stirring was measured. Data for a typical rate measurement are shown in Figure 2 and Table II.

Conductance Method. Rates of solution in acids of pH 3.1 and 4 were measured with an alternating current bridge and a conductance cell. The bridge consisted of two 1111-ohm decade boxes as fixed resistances, the conductance cell, and an 11,111-ohm decade box as a variable resistance. A small fixed transformer and a variable transformer fed the bridge with a current

Table II. Rate of Solution of Anhydrous Dicalcium Phosphate in 2.45×10^{-2} Molal Phosphoric Acid at 25° C.^a

Time, Min.	Mv. (Corr. for Heat of Stirring)	Wt. Dissolved, Mg.	Surface Area, Sq. Cm.	Wt. Dissolved, ^b Mg. Cm. ⁻²	Dissolution Rate, ^b (G. Cm. ⁻² Sec. ⁻¹) $\times 10^5$
0	8.310	...	922
0.25	8.5725	177.3	694	0.219	1.46
0.50	8.8050	334.4	666	0.450	1.54
0.75	9.0275	484.7	526	0.702	1.68
1.00	9.2000	601.3	460	0.939	1.58
1.25	9.3225	684.0	487	1.113	1.17
1.50	9.4450	766.8	401	1.299	1.24
1.75	9.5275	822.5	312	1.455	1.04
2.00	9.5900	864.8	239	1.609	1.03

^a Measured calorimetrically. Weight of salt, 1.0000 gram; weight of acid, 1200 grams. (1 mv. = 0.6756 gram salt dissolved)

^b Based on average surface area for time interval considered.

Table III. Rate of Solution of Anhydrous Dicalcium Phosphate in 1.12×10^{-3} Molal Phosphoric Acid at 25° C.^a

Time, Min.	Specific Conductance, (Ohm ⁻¹ Cm. ⁻¹) $\times 10^4$	Weight Dissolved, Mg.	Surface Area, Sq. Cm.	Weight Dissolved, ^b Mg. Cm. ⁻²	Dissolution Rate, (G. Cm. ⁻² Sec. ⁻¹) $\times 10^7$
0	3.951	...	46.1
1	3.093	6.9	40.9	0.159	26.50
2	2.645	11.8	37.7	0.283	20.66
3	2.401	14.7	35.0	0.363	13.33
4	2.253	16.8	33.3	0.424	10.17
5	2.173	17.7	32.5	0.452	4.67
6	2.123	18.5	31.8	0.477	4.17
7	2.099	18.7	31.6	0.483	1.00
8	2.088	18.8	31.5	0.486	0.50
9	2.076	19.0	31.5	0.492	1.00
10	2.073	19.1	31.3	0.496	0.67
15	2.079	19.7	30.8	0.515	0.63
30	2.095	19.8	30.8	0.518	0.033
60	2.103	19.9	30.7	0.521	0.017
90	2.107	20.0	30.6	0.525	0.022
120	2.112	20.0	30.6	0.525	0.00

^a Measured conductometrically. Weight of salt, 0.0500 gram; volume of acid, 125 ml.

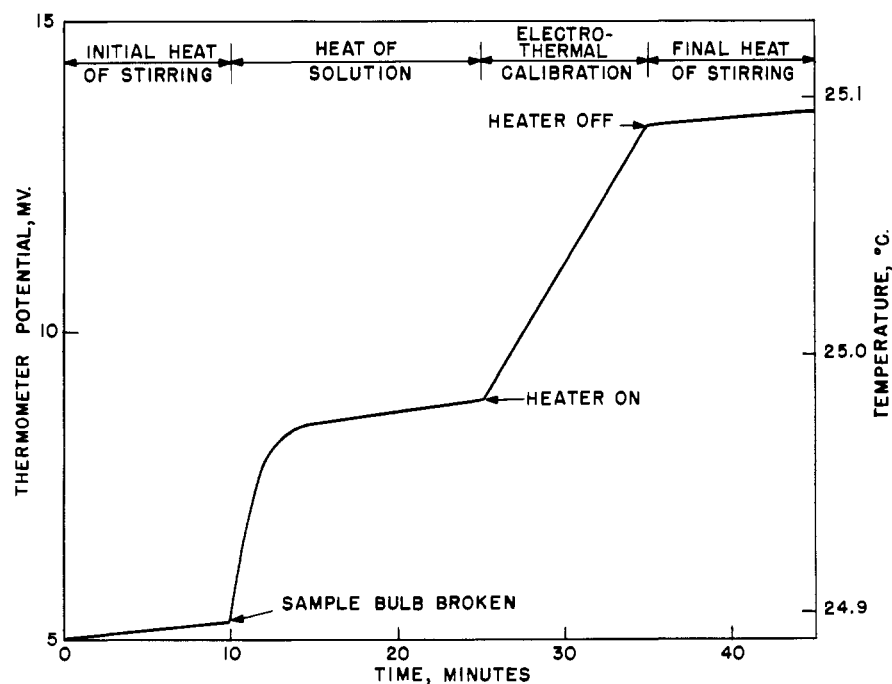


Figure 2. Typical record of calorimetric measurement of rate of solution

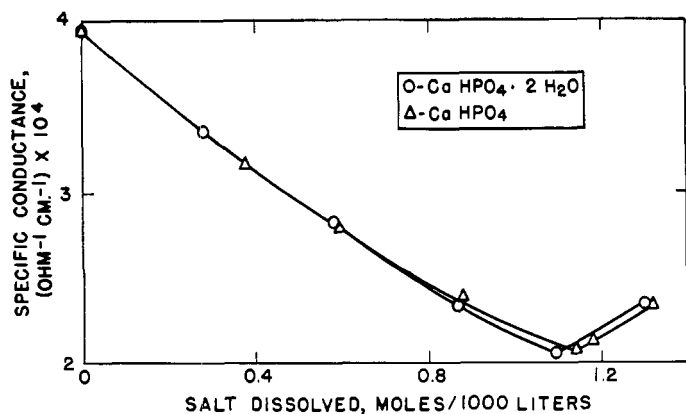


Figure 3. Specific conductance of solutions of dicalcium phosphate in 1.12×10^{-3} molal phosphoric acid at 25°C .

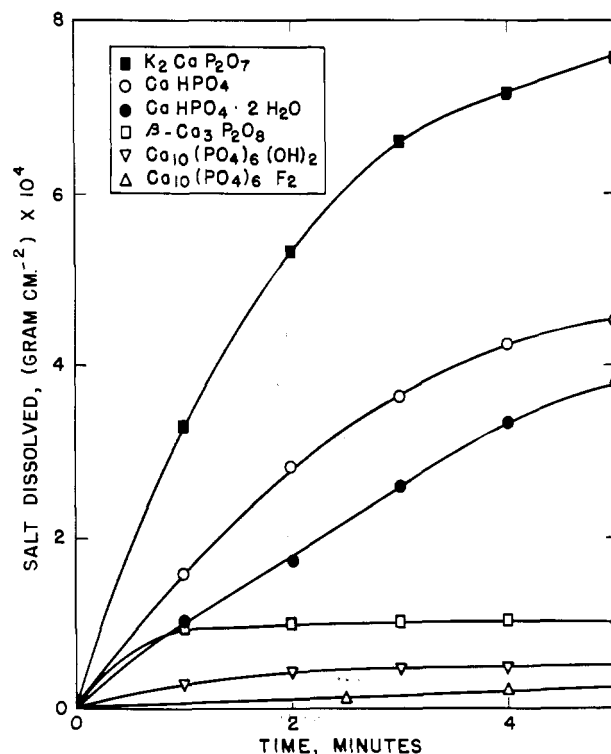


Figure 4. Rate of solution of calcium phosphates in 1.12×10^{-3} molal phosphoric acid at 25°C .

of 1.1 ma. from a 60-cycle 115-volt circuit. A null-point galvanometer indicated when the bridge was in balance.

The cell electrodes were platinized sheet platinum, 1 cm. square and 1 cm. apart. A constant-speed stirrer held the solids in suspension.

A rate measurement was made by adding 0.01 to 0.1 gram of salt to 125 ml. of solvent acid in the conductance cell, and measuring the rate of change of resistance of the solution. The resistance data were converted to specific conductance, L , $\text{ohm}^{-1} \text{cm.}^{-1}$, and the composition of the solution at any time was read from a calibration curve, such as those shown in Figure 3 for dicalcium phosphate. A calibration curve was required for each salt in each concentration of solvent acid. Typical conductance-rate data are shown in Table III.

Gravimetric Method. The rates of solution from cylinders of natural fluorapatite and of vitreous calcium metaphosphate were determined gravimetrically by measuring the loss of weight after rotation in a solvent acid for a measured time. The effect of stirring was determined by varying the speed of rotation.

Deposition of reaction products on the surface of the natural fluorapatite and calcium metaphosphate necessitated polishing of the specimens with 4/0 emery paper before each measurement.

Rate curves obtained by the gravimetric method were similar to those obtained by the other methods. The agreement between rates obtained with cylinders, the surface areas of which changed only slightly during a run, and rates obtained with powdered materials is evidence that the surface of the powdered materials was adequately known.

Results

Typical rate curves for the dissolution of synthetic fluorapatite, hydroxyapatite, β -tricalcium phosphate, dicalcium phosphate, and potassium calcium pyrophosphate in phosphoric acid of pH 3.1 are shown in Figure 4. The rate of solution of monocalcium phosphate monohydrate in this acid was roughly 50 times the highest rate of solution shown in Figure 4. The relative positions of the curves in Figure 4 are the same when the rates are expressed as grams of phosphoric oxide per square centimeter. The relative positions of the rate curves of the different salts were the same in acids of other pH in which rates were measured. In general, the curves of Figure 4 reflect the relative rates of solution of the salts, but the shapes of the curves are influenced markedly by experimental conditions, such as the ratio of the effective surface of the salt to the volume of the solvent. Therefore, the curves for the different salts are not comparable. Reliable approximate comparisons of different salts and of the effects of experimental conditions were made on the basis of "initial rates."

Data on the first 10 minutes of dissolution of four different salts in acids of pH 1 to 4 are shown in Figures 5 to 8. The initial portions of these curves are comparable, because the effect of concentration of the dissolved salt is not appreciable in this region. The plots bear out the earlier evidence (Figure 4) that the rates of solution of the salts are essentially in the same order as their

solubilities. The one exception is β -tricalcium phosphate, and uncertainties in the effective surface of this salt, as indicated before, may have been the cause of the discrepancy.

Rates of solution of Mexican and South American fluorapatite and of vitreous calcium metaphosphate, measured gravimetrically, are shown in Figure 9. During the first 5 hours, the rates of solution of the apatites were higher than that of the metaphosphate, as shown by the slopes of the curves, but the rates of solution of the apatites decreased considerably after 5 hours because of the change in composition of the liquid phase. The rate of solution of the metaphosphate, on the other hand, decreased slightly during the first hour and then remained almost constant at 2×10^{-8} gram $\text{cm.}^{-2} \text{sec.}^{-1}$ from the fifth hour to the end of the run at 249 hours (only 40 hours shown in Figure 9). The low initial crop response to the metaphosphate (37) could well be a reflection of the low initial rate of solution of the material. The prolonged constant rate of solution, if not altered by other factors in the soil, should be favorable to crop utilization of the fertilizer. The difference in behavior between the apatites and calcium metaphosphate suggests that the mechanisms of their dissolution are quite different.

In the following discussion, the "initial rate" is the substantially constant rate at the beginning of a rate curve. The extent of the period in which the rates are comparable depends upon the experimental conditions, and the initial-rate period ranged from 30 seconds to

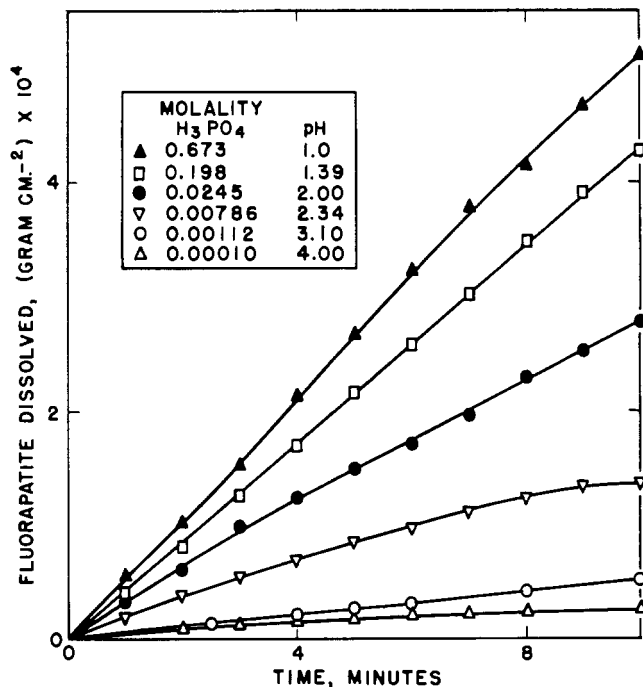


Figure 5. Dissolution of fluorapatite in phosphoric acid at 25° C.

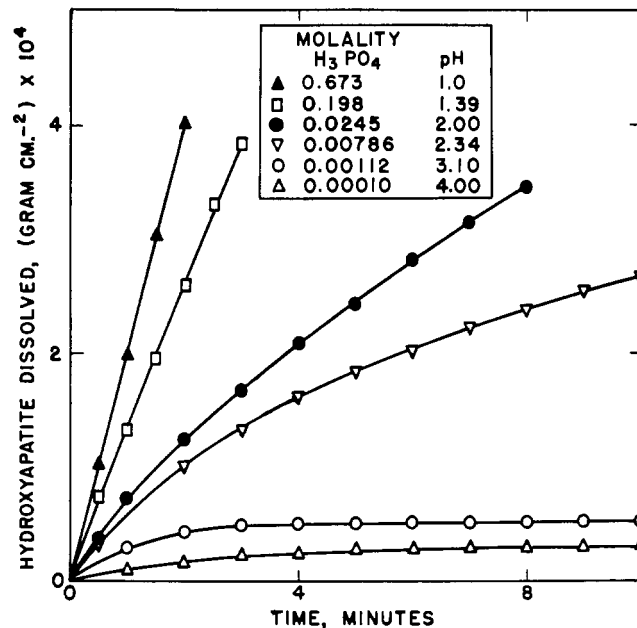


Figure 6. Dissolution of hydroxyapatite in phosphoric acid at 25° C.

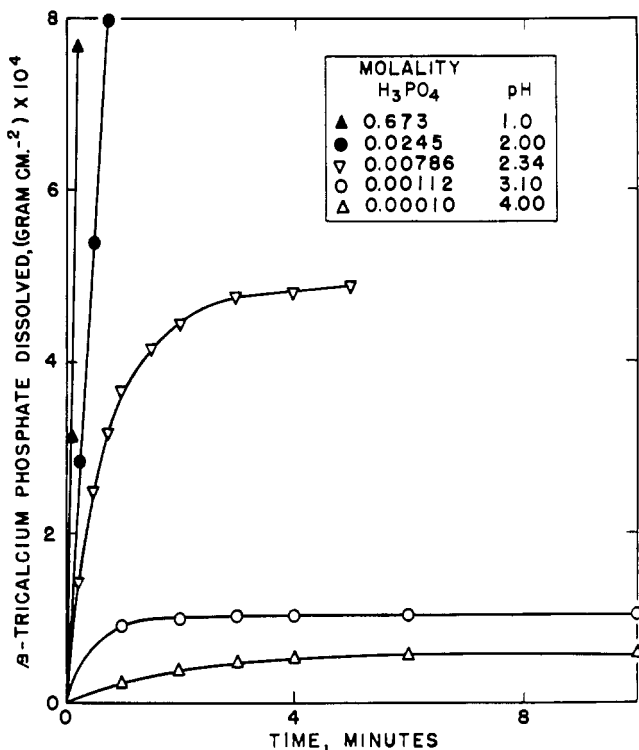


Figure 7. Dissolution of β -tricalcium phosphate in phosphoric acid at 25° C.

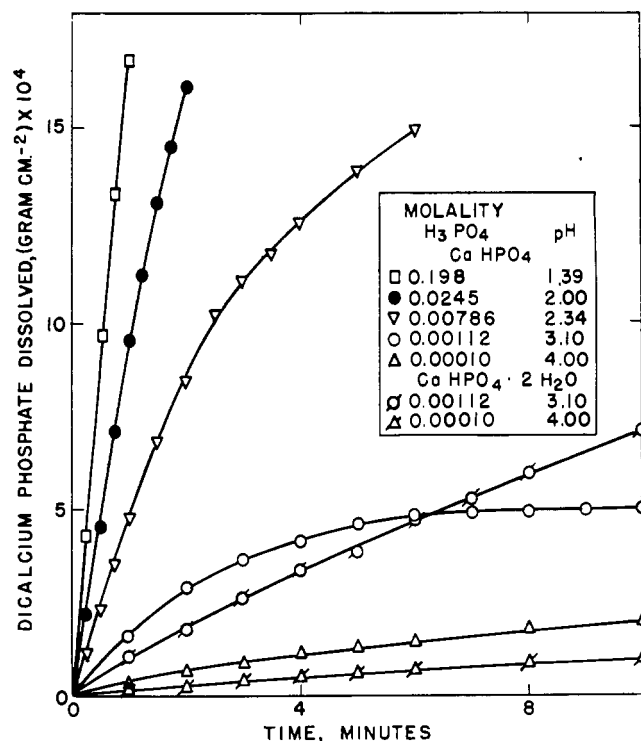


Figure 8. Dissolution of dicalcium phosphate in phosphoric acid at 25° C.

several minutes. In considering the kinetics and mechanism of the dissolution process, the effect of the change of concentration of the dissolved salt, with progress of dissolution, is discussed.

Effect of pH. The initial rates of solution of the calcium orthophosphates, V , gram cm.⁻² sec.⁻¹, as a function of the pH of the solvent can be represented by equations of the form

$$V = be^{apH} \quad (1)$$

where a and b are constants that are characteristic for each salt. The values of these constants and the initial-rate data used in the derivation of the equations for seven calcium phosphates are shown in Table IV. Hydrogen ions play an important part in the dissolution mechanism, as proved by the ob-

vious proportionality of the initial rate to their activity. A similar result is reported (25) for the dissolution of marble in acids.

The logarithms of the initial rates are plotted against the pH of the solvent in Figure 10. The hydrogen ion has less effect on the rate of solution of monocalcium phosphate than on any of the other materials, presumably because

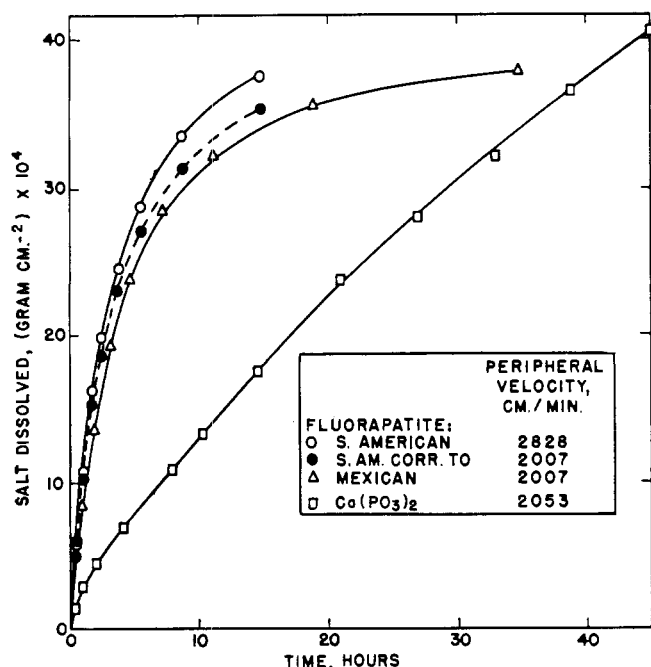


Figure 9. Dissolution of fluorapatite and calcium metaphosphate in 2.45×10^{-2} molal phosphoric acid at 25°C .

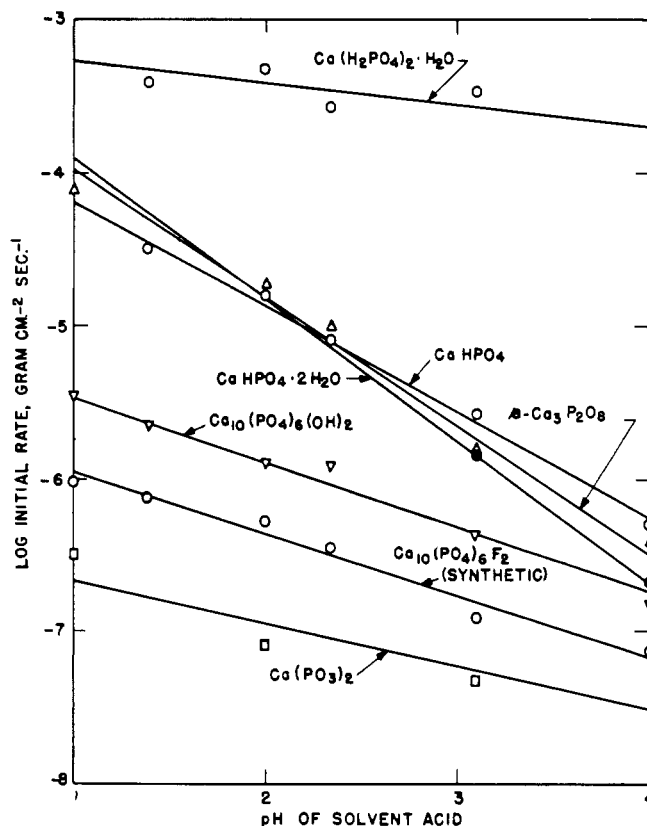


Figure 10. Effect of pH on initial rate of solution at 25°C .

Table IV. Initial Rates of Solution of Calcium Phosphates in Dilute Phosphoric Acid at 25°C .

Phosphate	Initial Rate of Solution, (Gram Cm. ⁻² Sec. ⁻¹) $\times 10^6$, at Indicated pH							Constants ^a		
	0.48	1.0	1.39	2.00	2.34	3.1	4	7	a	b $\times 10^6$
Fluorapatite										
Synthetic		0.970	0.730	0.530	0.347	0.118	0.0733	...	-0.956	2.93
Natural (S.A.)	3.96	1.82 ^b	...	0.385	0.207	...	0.0140 ^b	...	-1.624	9.25
Hydroxyapatite		3.50	2.30	1.33	1.24	0.424	0.147	...	-0.977	9.20
β -Ca ₃ P ₂ O ₈		76.3	...	18.8	9.53	1.58	0.382	...	-1.936	750
CaHPO ₄		67.2 ^b	31.8	15.6	7.88	2.65	0.517	...	-1.594	331
CaHPO ₄ ·2H ₂ O		132 ^b	...	15.3 ^b	...	1.43	0.206	...	-2.153	1130
Ca(H ₂ PO ₄) ₂ ·H ₂ O		540 ^b	393	474	274	351	206 ^b	...	-0.321	744
Ca(PO ₃) ₂		0.316	...	0.0785	...	0.0487	0.0307 ^b	0.00491	-0.654	0.420
K ₂ CaP ₂ O ₇		5.51

^a In Equation 1, $V = beapH$.

^b Calculated from Equation 1.

the monocalcium phosphate itself provides more hydrogen ions in dilute solution than do any of the other salts. The relation of the pH and concentration of monocalcium phosphate in phosphoric acid solutions has been reported (35). The effect of pH on the rate is greater for the dicalcium and tricalcium phosphates. For reasons that are not understood, the increasing effect of pH does not extend to the apatites.

Extrapolation of the curves for dicalcium and tricalcium phosphates leads to intersections with the hydroxyapatite line at pH's between 4 and 5. The more acid phosphates hydrolyze to yield less soluble, basic phosphates in this pH region, and hydrolysis may influence the observed rates of solution of these materials. The rates of hydrolysis of calcium phosphates to more basic, apatite-like phosphates undoubtedly have an important bearing on the behavior of

phosphate fertilizers in the soil (7).

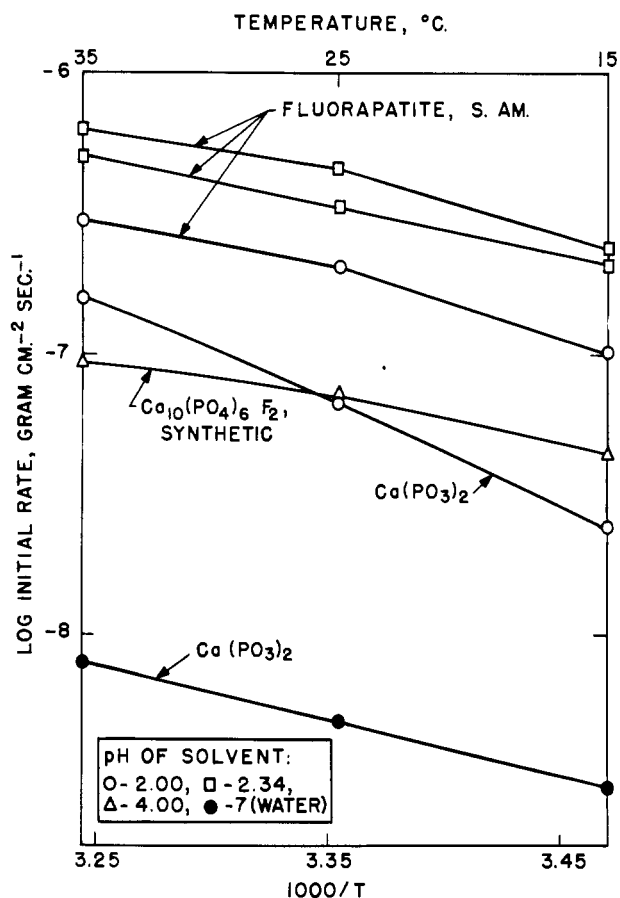
The increase in rate of solution of the calcium metaphosphate with increase in hydrogen ion activity (Figure 10) is in line with the effect of hydrogen ions on the rate of hydrolytic degradation of sodium polyphosphates (70).

Effect of Temperature. The effect of temperature on the initial rates of solution of fluorapatite and vitreous calcium

metaphosphate is shown in Figure 11. The values for the activation energies of the dissolution of calcium orthophosphates in acid solutions of pH 2 to 4 range from 6 to 9 kcal. per mole of salt, as derived from the slopes of curves like those of Figure 11 for fluorapatite. The activation energy decreases with increase in temperature, and this decrease is characteristic of diffusion in aqueous solu-

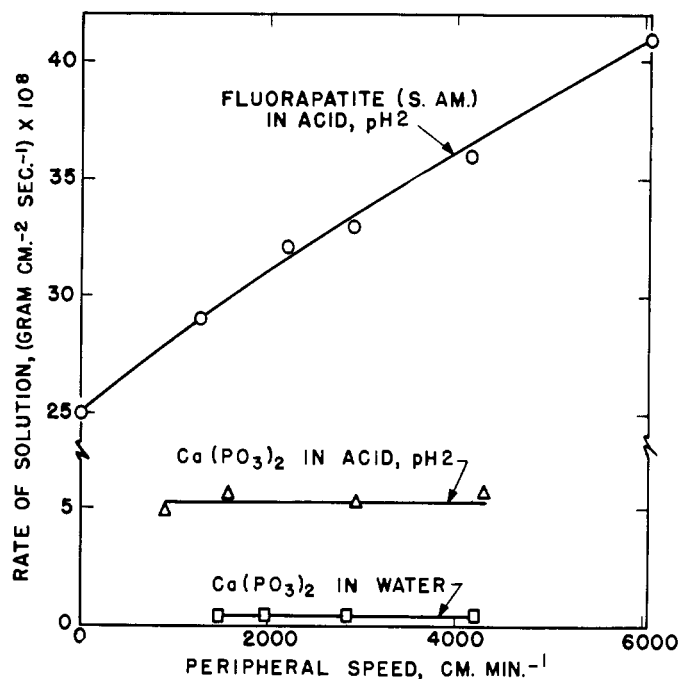
Table V. Viscosity and Density of Dicalcium Phosphate Solutions

pH of Initial Acid	Composition of Soln., Wt. %		Temp., °C.	Viscosity, Centipoises	Density, Grams/ML.
	CaO	P ₂ O ₅			
3.1	0.0056	0.015	15	1.139	0.99942
			25	0.891	0.99737
			35	0.723	0.99441
2.0	0.111	0.314	15	1.160	1.00303
			25	0.905	1.00098
			35	0.735	0.99811



▲ Figure 11. Effect of temperature on initial rate of solution of fluorapatite and calcium metaphosphate (synthetic fluorapatite measured conductometrically, others gravimetrically)

▼ Figure 12. Effect of agitation on initial rate of solution of cylinder specimens at 25° C.



tions (15, 24). The activation energy for the initial dissolution of calcium metaphosphate in phosphoric acid of pH 2, however, is between 16 and 20 kcal. per mole of calcium metaphosphate. The difference between the activation energies of the dissolution of the calcium orthophosphates and that of the metaphosphate is significant and indicates that the mechanism of the dissolution of the orthophosphates differs from that of the metaphosphate.

The energy of activation of the dissolution of calcium orthophosphates in dilute phosphoric acid solutions, 6 to 9 kcal. per mole of salt, is high enough to be that of a chemical reaction. However, the apparent energy of activation of a dissolution that is controlled by diffusion should be of this same magnitude. In the Nernst concept of a dissolution process controlled by diffusion (3), the chemical reaction at the surface of the solid is rapid and the liquid in contact with the solid is saturated with respect to the solid. When the liquid phase is stirred, there is a concentration gradient from saturation at the solid-liquid interface through a film with finite thickness to the concentration in the main body of the liquid phase. The thickness of the film, or the diffusion distance, varies directly with the viscosity of the liquid phase. But the viscosity of the calcium phosphate solutions varies inversely with

temperature, as shown in Table V for dicalcium phosphate solutions, and an increase in temperature causes a decrease in the diffusion distance and an increase in the rate.

The thickness of the diffusion film, in an unstirred liquid at 70° C., was found (14) to be about one third that at 20° C., from which it is estimated that the thickness decreases by about 2.2% per 1° C. rise in temperature. Combination of the effect of temperature on the thickness of the diffusion film with the effect of temperature on the coefficient of diffusion [an increase of 2.5% per 1° C. rise in temperature (14)] leads to a total increase in the rate of dissolution of 4.7% per 1° C. rise in temperature. This total effect corresponds to an activation energy of 7 kcal. per mole of salt, a value in good agreement with those found for the energy of activation of the dissociation of calcium orthophosphates in dilute phosphoric acid solutions. Temperature coefficients of the same magnitude were reported (24, 25) for other materials whose rates of dissolution were shown to be controlled by diffusion. Further evidence that diffusion controls the rate of solution of the calcium orthophosphates was obtained from a study of the effect of the degree of agitation on the rate of solution.

The activation energy for dissolution of the calcium metaphosphate in dilute

phosphoric acid solutions ranged from 16 to 20 kcal. per mole of calcium phosphate, the order of magnitude of activation energies of processes that are controlled by chemical reactions in aqueous solutions. The energy of activation of the hydrolysis of calcium metaphosphate glass in orthophosphoric acid solutions of pH 2.34 and 2.0 at 60° and 70° C. ranged from 17 to 25 kcal. per mole of calcium metaphosphate. Activation energies of 22 to 31 kcal. per mole were reported (6) for the hydrolysis of pyrophosphate. The calcium phosphate glass with the so-called "metaphosphate" composition contains polymers—probably predominantly linear polymers. It is postulated that the ends of these chains undergo hydrolytic degradation in the dissolution process. Hydrolysis probably is the mechanism that controls the rate of solution of calcium metaphosphate in phosphoric acid solutions of pH 2. This difference in mechanism for the dissolution of the orthophosphate crystals and the polymeric metaphosphate is in harmony with the structural difference in the two phosphates. The degradation of the polymer involves the breaking of a distinctly different kind of bond from that found in crystalline orthophosphates.

The activation energy found for the rate of solution of calcium metaphosphate in water was 9 kcal. per mole. This

value is compatible with control by diffusion, but other experimental evidence shows that the process is not controlled by diffusion.

Effect of Stirring. The effect of the speed of rotation of cylinder specimens on the rate of dissolution of a natural fluorapatite and of vitreous calcium metaphosphate is shown in Figure 12. The curve for fluorapatite is typical of the behavior of the calcium orthophosphates.

Increase in shear at the solid-liquid interface increased considerably the rate of dissolution of the calcium orthophosphates in all the solvents studied. The results obtained with the natural fluorapatites are characteristic of processes that are controlled by diffusion (3, 14, 24, 25, 31, 32) and these results are considered proof that the rates of dissolution of calcium orthophosphates are controlled by diffusion.

The rate of dissolution of vitreous calcium metaphosphate in water or in dilute phosphoric acid solution is not affected by the speed of rotation (Figure 12). The results are considered proof that the dissolution of calcium metaphosphate is not controlled by diffusion.

Kinetics

The experimental results showed that the rates of solution of the calcium orthophosphates are controlled by diffusion. Theoretical treatments of the transport of heat and matter by diffusion are available (7, 19, 23). Noyes and Whitney (32) were the first to apply the theory to a dissolution which they showed was controlled by diffusion. Their assumptions regarding diffusion-controlled dissolution lead to the equation

$$dC/dt = k(C_0 - C) \quad (2)$$

where

C = concentration of solute at time t

C_0 = concentration of solute at saturation

k = rate constant for the specific experimental conditions

As the rate of change of concentration varies directly with the amount of reactant surfaces, S , and inversely with the volume of solvent, V , the rate constant, k' , for a unit area of surface in a unit volume of solvent is

$$k' = kV/S \quad (3)$$

Nernst (37) advanced the hypothesis that the constant k for a diffusion-controlled reaction is related to the diffusion coefficient, D , as in the expression

$$k = DS/\delta V \quad (4)$$

where δ is the distance of diffusion. The validity of this hypothesis, particularly the magnitude of values usually used for δ , has been questioned (30, 38, 41). Most values of δ calculated on the basis of the Nernst assumptions for a variety

Table VI. Variation of Rate Constant, k' , with Degree of Saturation of Solvent^a

Time, Min.	Fluorapatite		Anhydrous Dicalcium Phosphate	
	C/C_0	$k' \times 10^3$	C/C_0	$k' \times 10^3$
1	0.08	1.4	0.30	18
2	0.14	1.3	0.53	21
3	0.19	1.2	0.66	21
4	0.24	1.1
5	0.27	1.1	0.79	20
7	0.33	1.0
8	0.84	15
10	0.40	0.8	0.85	13
20	0.50	0.6
30	0.60	0.5
90	0.75	0.3

^a Synthetic fluorapatite and anhydrous dicalcium phosphate dissolving in 1.12×10^{-3} molal phosphoric acid at 25° C.

of chemical reactions which may be controlled by diffusion, however, are in the range 10^{-3} to 10^{-2} cm. Glasstone (14) presented experimental evidence that the diffusion distance remains approximately in this range with variation in temperature and degree of agitation.

In an application of the Noyes and Whitney and the Nernst hypotheses to the present measurements, data for the rate of dissolution of synthetic fluorapatite and anhydrous dicalcium phosphate in 1.12×10^{-3} molal phosphoric acid solution (pH 3.1) were used to calculate the values of k' shown in Table VI. Values for k were calculated by use of the integrated form of Equation 2, and values of k' were calculated by use of Equation 3.

The decrease in k' with time, especially for fluorapatite, shows that the rate process is not represented adequately by Equation 2. This result is characteristic of most of the rate measurements with orthophosphates. Constant k' for dicalcium phosphate remains essentially unchanged up to 80% of saturation. The range of constancy of k' varied from about 25 to 80% of the way to saturation, depending upon the salt and the concentration of the solvent acid.

Several phenomena associated with the dissolution of calcium phosphates would result in variation in k' as the dissolution proceeds, even though the rate is controlled by diffusion. As several of the calcium phosphates hydrolyze, and even the apatites do not necessarily dissolve congruently (27, 39), C_0 is not constant over the entire range of dissolution. Incongruent dissolution of fluorapatite and of potassium calcium pyrophosphate was observed in the rate measurements, and new solid phases—i.e., calcium fluoride and anhydrous dicalcium phosphate, respectively—appeared in the residues. The mechanism is not understood in sufficient detail to permit development of expres-

sions for the variation of C_0 with extent of dissolution. The diffusion coefficients of salts are not constant over a wide range of concentration. Although the rate of solution is controlled by diffusion, the simple first-order rate, Equation 2, should not be expected to fit the experimental data over the entire range of concentration.

Diffusion coefficients were calculated from the initial rate constants for several of the calcium phosphates. The diffusion distance, δ , was evaluated for the calorimetric and conductometric measurements by use of Equation 4 and a value of D for hydroxyapatite that was determined independently by a gravimetric porous-disk method (40). The calculated diffusion coefficients, shown in Table VII, are only approximate, but the agreement in magnitude with diffusion coefficients of other salts in aqueous solution (5, 18) supports the conclusion that the rates of solution are controlled by diffusion.

Equation 2 can be modified empirically to fit the experimental data. An example of such a modification for the rate of solution of fluorapatite is

$$k = \frac{2.303}{t^n} \log \frac{C_0(1 + at^{1/2})}{C_0(1 + at^{1/2}) - C} \quad (5)$$

where a , n , and k are empirical constants, and the other symbols are the same as in Equation 2. Rate constant k in Equation 5 does not have the same relation to the diffusion coefficient as does the k of Equation 2. Values for a , n , and k for the dissolution of synthetic fluorapatite in phosphoric acid solutions of pH 3.1 and 4 are shown in Table VIII. Extensive empirical representation of the rate data from this study was not attempted because of the limited usefulness of such equations.

Conclusions

The rates of solution of the calcium phosphates vary inversely with the pH

Table VII. Specific Rates of Dissolution and Diffusion Coefficients of Calcium Phosphates in Phosphoric Acid at 25° C.

Phosphate	Solvent Acid			Time, Sec.	Concn. of Solute, Grams/Liter		Surface Area of Salt, Sq. Cm.	Stirrer Speed, R.P.M.	Diffusion Distance, Cm. × 10 ³	Specific Rate k' × 10 ³	Calcd. Diffusion Coeff. D, (Sq. Cm./Sec.) × 10 ⁶
	Molality H ₃ PO ₄	pH	Vol., ml.		C ₀	C					
Ca ₁₀ (PO ₄) ₆ F ₂	0.0001	4.0	125	120	0.025	0.0009	12.3	1180	1.73	3.00	5.2
	0.00112	3.1	125	60	0.086	0.0070	123	1180	1.73	1.43	2.5
	0.00786	2.34	1200	90	0.539	0.0312	1217	458	2.76	0.66	1.8
	0.0245	2.00	1200	180	1.327	0.0487	590	458	2.76	0.42	1.2
	0.198	1.39	1200	45	8.553	0.0336	1212	458	2.76	0.085	0.23
	0.673	1.00	1200	45	21.255	0.0439	1208	458	2.76	0.045	0.12
Ca ₁₀ (PO ₄) ₆ (OH) ₂	0.0001	4.0	125	60	0.031 ^a	0.0026	38	1180	1.73	4.80	8.3
	0.00112	3.1	125	60	0.104 ^a	0.0448	192	1180	1.73	6.11	10.6
	0.00786	2.34	1200	60	0.6150	0.0555	979	458	2.76	1.91	5.3
	0.0245	2.00	1200	45	1.6864	0.1950	3900	458	2.76	0.84	2.3
	0.198	1.39	1200	150	10.2054	0.7317	2635	458	2.76	2.25	6.2
β-Ca ₃ P ₂ O ₈	0.0001	4.0	125	60	0.0150	0.00424	23.1	1180	1.73	30.1	51.8
	0.0001	4.0	125	120	0.0150	0.00704	22.9	1180	1.73	28.8	49.8
	0.0001	4.0	125	120	0.0150	0.00592	23.0	858	2.19	22.7	49.8
	0.0001	4.0	125	120	0.0150	0.00432	23.1	484	3.25	15.3	49.8
	0.00112	3.1	125	60	0.1003	0.0809	111	1180	1.73	30.8	53.6
	0.00112	3.1	1200	15	0.1003	0.0292	1422	458	2.76	19.4	53.5
	0.00786	2.34	1200	15	0.6242	0.2533	2130	458	2.76	19.5	54.0
	0.0245	2.00	1200	15	0.8263	0.4416	1874	458	2.76	29.8	82.2
	CaHPO ₄	0.0001	4.0	125	120	0.0520	0.00448	9.0	1180	1.73	10.4
	0.00112	3.1	125	60	0.1790	0.0552	43.5	1180	1.73	17.6	30.4

^a Calculated on assumption that C₀ for hydroxyapatite is 1.2 times C₀ for fluorapatite in same solvent.

of the solvent acid; therefore, hydrogen ions play an important role in the chemical reaction. At solvent acid pH's between 1 and 4, the relative rates for the different calcium orthophosphates are essentially in the same order as their solubilities. The effects of temperature, stirring, and salt compositions of the orthophosphates indicate that, at a given pH, the rate of solution is controlled by diffusion. The diffusion phenomenon is complicated by incongruent solubility and by changes in ionic species with concentration.

The rate of solution of vitreous calcium metaphosphate is controlled by the rate of a chemical reaction, probably hydrolytic degradation of polymeric phosphate chains.

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Table VIII. Constants in Empirical Equation 5 for Rate of Solution of Synthetic Fluorapatite in Phosphoric Acid at 25° C.

Molality H ₃ PO ₄ in Solvent Acid	a	n	k, Sec. ⁻ⁿ × 10 ³
0.00010	-0.005	0.875	7.4 ± 0.2
0.00112	-0.005	1.128	0.274 ± 0.004

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BORON SUPPLEMENTS

Response of Alfalfa to Applications of a Soluble Borate and a Slightly Soluble Borosilicate Glass

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Boron response of Ranger alfalfa grown from Evesboro sandy loam to additions of a coarsely ground experimental borosilicate glass has been compared to that of borax under greenhouse conditions. The concentration of boron in the plant tended to become approximately proportional to application and to reach a minimum value, in each treatment, during late summer growth. Significant increases in yield were produced by borax from 5 to 80 pounds and by glass from 12 to 360 pounds per acre, indicating that a material of intermediate solubility could be used to better advantage.

SOIL-BORON DEFICIENCIES are, ordinarily, corrected by the application of sodium tetraborate in the form of borax, the decahydrate, or fertilizer borate, the pentahydrate. These compounds are not entirely satisfactory for this use, and the difficulties experienced are associated with the circumstance that the solubilities of sodium borates exceed so very greatly the optimal boron concentration needed in soil solution for healthy vegetative growth. Although plants, generally, require boron as a nutrient in small amounts, they are very sensitive to the element. An excess in soluble form may seriously impair plant growth and there is an ever-present danger in application of localized high concentrations. Furthermore, the high solubility of the compounds now in use makes them very susceptible to rapid losses from the root zone by leaching. In boron-deficient areas, frequent small applications are often used in order to maintain the concentration in soil solution at a level suitable for crop production.

The possible advantages of slightly soluble substances, as carriers of boron (or other trace nutrients), has been the subject of a number of recent investi-

gations (4-8, 17). Borosilicate glass is of special interest, as its solubility behavior can be adjusted over a broad range of varying chemical composition. Studies with this type of carrier showed that some glasses do supply boron and may be used in relatively large amounts without producing toxicity.

The application of supplemental boron to a light soil in the form of a coarsely ground borosilicate glass at two different degrees of fineness has been compared to equivalent treatments with borax for growth of alfalfa under greenhouse conditions. Response of the crop to these materials is reported in terms of yield and boron content.

Culture Preparation and Management

Soil. Evesboro sandy loam was weighed out in 7.5-pound portions which were placed in No. 10 plastic-coated metal cans serving as plant pots. In a lime treatment, equal molecular amounts of calcium hydroxide and magnesium oxide, equivalent in total to 2200 pounds of calcium carbonate per acre (weight basis), were mixed thoroughly with the soil. The cultures were kept in a moist condition for 4 weeks to permit equilibration with the lime; the average pH attained was 6.9. The general fertility status was raised at this time to a suitable level for good growth by

mixing the cultures with the equivalent of:

Chemical	Pounds/Acre (Area Basis)
N	200
P ₂ O ₅	300
K ₂ O	200
CuSO ₄ ·5H ₂ O	5
ZnSO ₄ ·7H ₂ O	5
MnCl ₂ ·4H ₂ O	15
MoO ₃	1

Supplemental potassium, equivalent to 100 pounds of potassium oxide per acre, was added shortly after the second harvest. The chemicals used to effect each of the above basal treatments were substantially boron-free, as shown by analysis prior to use.

Boron Carriers. The chemical compositions of the boron-containing substances were as follows:

Constituent	Carrier, % of Total	
	Borax ^a	Glass 176-C ^b
B ₂ O ₃	36.52	14.25
SiO ₂	...	52.81
Fe ₂ O ₃	...	0.07
Al ₂ O ₃	...	8.11
CaO	...	5.00
K ₂ O	...	4.39
Na ₂ O	16.25	14.00
H ₂ O	47.24	...

^a Theoretical composition.

^b Values determined by analysis. Glass supplied by J. A. Naftel, Pacific Coast Borax Co.

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