

601. *The Phosphates of Calcium. Part V.* Revision of the Earlier Space Diagram.*

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The author's original diagram of the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ has been revised.

It is fifty years since a space diagram of the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ was published.¹ Many data needed to represent the system exactly were then lacking, but most have since been gathered. A new diagram which is essentially true to scale can thus be constructed; it justifies the older one satisfactorily in spite of some minor modifications.

EXPERIMENTAL

Solubilities were determined by standard procedures in silica vessels. Equilibrium solutions were analysed gravimetrically, as were the solid calcium phosphates after being washed with water, acetone, and ether to remove mother liquor and solid phosphoric acids. The calcium phosphates were also examined microscopically. The composition of the solution decided between the three acids $\text{H}_8\text{P}_2\text{O}_9$, H_3PO_4 , and $\text{H}_4\text{P}_2\text{O}_7$. When determining solubilities of the phosphoric acids themselves, not only were the equilibrium solutions analysed but also the crystals of acid after separation as completely as possible from the solution. This was as a check against the possible appearance of some new and unexpected acid, but it also gave a valuable distinction between points on the normal H_3PO_4 or $\text{H}_4\text{P}_2\text{O}_7$ curves and points on the retroflex portions of the $\text{H}_8\text{P}_2\text{O}_9$, H_3PO_4 , and $\text{H}_4\text{P}_2\text{O}_7$ curves. Where the solution point was on a normal branch, the crystals would contain more P_2O_5 than the solution, but when it was on the retroflex parts of the curves the crystals would contain less P_2O_5 than the solution.

Phosphoric oxide was weighed as $\text{Mg}_2\text{P}_2\text{O}_7$ after preliminary separation with molybdate when necessary and calcium oxide as such after precipitation as oxalate. It was found essential to determine and allow for the small amount of phosphoric oxide present in the calcium oxide. In analyses of phosphoric acids all solutions were digested with a few c.c. of 2N-hydrochloric acid for at least $\frac{1}{2}$ hr. before precipitation with magnesia mixture. Solids and solutions containing calcium oxide and over 60% of phosphoric acid were digested with nitric acid for some time before separation of phosphomolybdate precipitates.

The Boundaries of the Ice Field.—Freezing points of phosphoric acid solutions. A Beckmann thermometer and apparatus with a magnetic stirrer were used for the readings above -4° and

* Part IV, *J.*, 1917, **111**, 620.

¹ Bassett, *Z. anorg. Chem.*, 1908, **59**, 29.

a pentane thermometer which was also the stirrer for lower temperatures, obtained by means of solid carbon dioxide and acetone in a Dewar vessel. Several readings of the f. p. were taken in each case with decreasing amounts of supercooling; the accepted value was that obtained after least supercooling. Disturbance caused by heating of the coil of the electromagnet was overcome by winding fine lead tubing, through which cold water passed, over the coil. Solution for analysis was removed with a cooled pipette having a detachable filter bulb containing glass wool. Freezing points, with percentages of P_2O_5 in parentheses, were: -0.389° (1.088), -1.551° (4.690), -3.315° (8.999), -18.5° (25.86), -30.0° (31.31), -65.0° (41.01). By extrapolation the ice- $H_8P_2O_9$ cryohydric point is -100.0° and 46.2% of P_2O_5 .

The freezing-point curve of $H_8P_2O_9$ solutions was determined by Ross and Jones² who considered that the cryohydric point was at -85° with 45.29% of P_2O_5 . This is out of step with their other points on the solubility curve of $H_8P_2O_9$, but falls well on the freezing-point curve as shown in their paper and with the present results. It seems that Ross and Jones mistook the condition of extreme glassy viscosity prevailing at -85° for a complete cryohydric crystallisation; their curves indicate -100° as the most probable cryohydric temperature.

Solutions in equilibrium with ice and either calcium hydroxide or one or two of the calcium orthophosphates. These are described in Table I

Solubilities of the Phosphoric Acids.—The complete solubility curve of $H_8P_2O_9$ agrees well with the results of Smith and Menzies³ and of Ross and Jones.² A few points on both the normal and retroflex portions of the H_3PO_4 curve were obtained and agree well with Ross and

TABLE I.

Temp.	Solution		Solid other than ice		Nature of solids other than ice
	CaO (%)	P_2O_5 (%)	CaO (%)	P_2O_5 (%)	
-0.116°	0.130	—	—	—	Coarse crystals of $Ca(OH)_2$ *
These three quintuple points would be very close together over a very small range of temperature and of CaO and P_2O_5 concentration ^b					
-2.6	3.235	9.513	33.00	41.11	Ca(OH) ₂ and hydroxyapatite Hydroxyapatite and $Ca_3P_2O_8, xH_2O$ $Ca_3P_2O_8, xH_2O$ and $CaHPO_4, 2H_2O$ $CaHPO_4, 2H_2O$
-5.5	5.251	16.25	32.62	41.20	
-7.0	5.819	18.33	32.60	41.34	
-7.5	6.10	19.62	29.91	43.74	CaHPO ₄ , 2H ₂ O and CaH ₄ P ₂ O ₈ , H ₂ O *
-7.5	6.07	19.5	—	—	CaH ₄ P ₂ O ₈ , H ₂ O " " †
-8.0	5.883	19.86	22.77	56.20	" " " " †
-9.5	5.47	21.10	22.67	55.90	" " " " †
-20.0	3.638	28.95	22.67	56.09	" " " " †
-40.0	1.657	35.40	22.54	56.44	" " " " †
-100	trace	46.2	—	—	CaH ₄ P ₂ O ₈ , H ₂ O and $H_8P_2O_9$, by extrapolation

* Bassett, *J.*, 1934, 1270. ^b Bassett, *J.*, 1917, 111, 620.

† Direct determination of the quintuple point. The solid phase analysed was slightly moist.

‡ Quintuple point determined graphically as the point of intersection of the three curves: ice- $CaHPO_4, 2H_2O$, ice- $CaH_4P_2O_8, H_2O$, and $CaHPO_4, 2H_2O$ - $CaH_4P_2O_8, H_2O$. The actual plots were of the three temperature- P_2O_5 and temperature-CaO curves corresponding to these.

Jones's figures, which only extended to the m. p. of H_3PO_4 . Sufficient points were also determined to give an approximate indication of the $H_4P_2O_7$ solubility curve for which the only previous figure was the m. p.⁴ but no great accuracy is claimed. Our cooling system gave very steady temperatures and mixtures reached equilibrium in 1—2 hr. The lowest temperature at which the solubility of $H_8P_2O_9$ could be determined was -66° owing to the very high viscosity and it was difficult to obtain even 0.5 g. for analysis with the cooled pipette with filter bulb. The crystals could not be separated for examination until the temperature had risen to -45° . There was no indication that this changed the character of the crystals or that they were other than $H_8P_2O_9$.

Merck's syrupy phosphoric acid (64—65% of P_2O_5) was used for the solubility work on $H_8P_2O_9$, somewhat concentrated in platinum where necessary. Acids in the H_3PO_4 range were prepared by heating the syrupy acid in a platinum basin to temperatures not above 120° and acids in the $H_4P_2O_7$ range by heating the syrupy acid with redistilled $POCl_3$ to not above

² Ross and Jones, *J. Amer. Chem. Soc.*, 1925, 47, 2165.

³ Smith and Menzies, *J. Amer. Chem. Soc.*, 1909, 31, 1183.

⁴ Giran, *Compt. rend.*, 1908, 146, 1270.

200°. ⁵ Acids so prepared had been kept for many months before being used for the solubility determinations.

Three experiments are included in Table 2, in two of which $\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$ and $\text{H}_8\text{P}_2\text{O}_9$,

TABLE 2.

Temp.	Solution P_2O_5 (%)	Moist solid P_2O_5 (%)	Nature of solid phase	Temp.	Solution P_2O_5 (%)	Moist solid P_2O_5 (%)	Nature of solid phase
-100°	46.2	—	Ice and $\text{H}_8\text{P}_2\text{O}_9$ (by extrapn.)	25°	68.82	70.66	H_3PO_4
-66	48.76	60.98	$\text{H}_8\text{P}_2\text{O}_9$	37.3	71.30	71.52	"
-53	49.10	65.06	"	37.35	71.52 ^e	—	H_3PO_4 and $\text{CaH}_4\text{P}_2\text{O}_8$
-35	51.26	62.42	"	37.6	71.5	—	H_3PO_4
0	57.50	65.09	"				
0	57.20	—	$\text{H}_8\text{P}_2\text{O}_9$ and $\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$	42.35 ^f	72.45	72.45	—
3	57.60	63.50	$\text{H}_8\text{P}_2\text{O}_9$	35.75	74.05	—	H_3PO_4
14.7	60.32	65.13	"	25	{ 77.06 ^g	76.49	"
25	63.02 ^b	—	$\text{H}_8\text{P}_2\text{O}_9$ and $\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$		{ 77.02 ^h	—	"
26.25	63.55	65.83	$\text{H}_8\text{P}_2\text{O}_9$	33.3	76.28	—	$\text{H}_4\text{P}_2\text{O}_7$
28.5	64.32	65.73	"	38	76.41	—	"
29.35	66.35	66.35	M. p. of $\text{H}_8\text{P}_2\text{O}_9$ ^e	41.5	76.64	77.00	"
29	67.03	—	$\text{H}_8\text{P}_2\text{O}_9$	61 ⁱ	79.77	79.77	—
27.7	67.86	66.52	"	50.8	81.22	—	$\text{H}_4\text{P}_2\text{O}_7$
25	68.44	67.24	"	50	81.00	—	"
23.5	68.64	—	$\text{H}_8\text{P}_2\text{O}_9$ and H_3PO_4 ^d	47.1	81.11	—	"

^a +0.112% of CaO. ^b +0.204% of CaO. ^c Estimated from curve. ^d Eutectic; Ross and Jones (ref. 2). ^e + trace of CaO. ^f M. p. of H_3PO_4 (refs. 3 and 2). ^g After 4 weeks. ^h After 13 months. ⁱ M. p. of $\text{H}_4\text{P}_2\text{O}_7$ (ref. 4). Values in italics are from other sources.

were present as solid phases and in the other $\text{CaH}_4\text{P}_2\text{O}_8$ and H_3PO_4 . The solubility of the calcium phosphate in the concentrated acids is so small as hardly to affect the P_2O_5 content of the solutions.

Other data used in constructing the space diagram. These are shown in Table 3. We also used the 25°, 40°, and 50.7° isothermals previously published¹ as well as the figures for the quintuple point at 152° (5.60% of CaO; 53.00% of P_2O_5).

TABLE 3.

Solution		Nature of solid phase	Solution		Nature of solid phase
CaO (%)	P_2O_5 (%)		CaO (%)	P_2O_5 (%)	
0° Isothermal			25° Isothermal		
—	57.50	$\text{H}_8\text{P}_2\text{O}_9$	0.204	63.02	$\text{H}_8\text{P}_2\text{O}_9$ and $\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$
0.112	57.20	$\text{H}_8\text{P}_2\text{O}_9$ and $\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$	5.885	24.40	$\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$ and CaHPO_4
0.716	46.94	$\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$			(stable)
2.859	35.40	"	6.58	22.62	$\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$ and $\text{CaHPO}_4, 2\text{H}_2\text{O}$ (metastable)
4.482	27.96	"			
6.008	20.55	$\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$ and $\text{CaHPO}_4, 2\text{H}_2\text{O}$			50° Isothermal
4.822	15.47	$\text{CaHPO}_4, 2\text{H}_2\text{O}$	5.770	29.56	$\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$ and CaHPO_4
2.23	6.365	"			

The solution saturated with respect to H_3PO_4 at 37.3° contained 71.30% of P_2O_5 , while when both solid H_3PO_4 and $\text{CaH}_4\text{P}_2\text{O}_8$ were present at 37.35° the solution contained 71.52% of P_2O_5 and only a trace of CaO. At 35.75° in contact with saturated solution and solid H_3PO_4 there was also no tendency for $\text{CaH}_4\text{P}_2\text{O}_8$ to become hydrated. These facts indicate that the quintuple point with solid phases H_3PO_4 , $\text{CaH}_4\text{P}_2\text{O}_8$, and $\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$ is not at 39° as originally suggested but probably at as low a temperature as 30°. The $\text{CaH}_4\text{P}_2\text{O}_8$ - $\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$ boundary curve would then miss the solubility curve of $\text{H}_8\text{P}_2\text{O}_9$ by a reasonable margin before meeting that of H_3PO_4 at a point corresponding to 30° and 69.8% of P_2O_5 and a trace of CaO which may be taken as the co-ordinates of the quintuple point with solid phases H_3PO_4 , $\text{CaH}_4\text{P}_2\text{O}_8$, and $\text{CaH}_4\text{P}_2\text{O}_8, \text{H}_2\text{O}$.

The Boiling Line.—Data are given in Table 4. The solubility of $\text{Ca}(\text{OH})_2$ at 100° is that of coarse crystals and obtained from the solubility curve given by Bassett.⁶ The figures for

⁵ Geuther, *J. prakt. Chem.*, 1874, **8**, 359.

⁶ Bassett, *J.*, 1934, 1270. (The reference to Shenstone and Cundall in line 8 from bottom of p. 1270 is given incorrectly and should be *J.*, 1888, **53**, 550.)

the basic phosphates are taken from Part IV⁷ and those for the hydrogen orthophosphates from Part III¹ (where the CaO content of the solution boiling at 169° is given erroneously as 4.489% though the correct figure, 3.489%, was plotted).

TABLE 4.

Temp.	Solution CaO (%)	P ₂ O ₅ (%)	Nature of solid phase
ca. 100°	0.517	—	Ca(OH) ₂
"	0.0561	Trace	Ca(OH) ₂ and hydroxyapatite
"	0.00001	0.000012	Hydroxyapatite
"	0.0416	0.115	Hydroxyapatite and Ca ₃ P ₂ O ₈ ·xH ₂ O
"	0.0474	0.133	Ca ₃ P ₂ O ₈ ·xH ₂ O and CaHPO ₄
115	5.623	43.60	CaHPO ₄ and CaH ₄ P ₂ O ₈ ·H ₂ O
132	4.327	53.43	CaH ₄ P ₂ O ₈ ·H ₂ O and CaH ₄ P ₂ O ₈
169	3.489	63.95	CaH ₄ P ₂ O ₈
200	2.404	67.29	CaH ₂ P ₂ O ₇
220	1.950	69.56	CaH ₂ P ₂ O ₇

The data for CaH₂P₂O₇ have not been published before. The value 220° is somewhat uncertain owing to superheating. The plot of boiling points against composition suggests that the boiling line cuts the boundary between the fields of CaH₄P₂O₈ and CaH₂P₂O₇ only a little above 169° and possibly at about 175°.

The solid phases from the experiments at 200° and 220° were obtained readily for analysis by filtration on asbestos in a small Buchner funnel and, after cooling, washing well with acetone and then ether (Found, at 200°: CaO, 26.12; P₂O₅, 65.56; loss on ignition 9.00. Found, at 220°: CaO, 25.97; P₂O₅, 65.56; loss on ignition 9.28. Calc. for CaH₂P₂O₇: CaO, 25.92; P₂O₅, 65.74; H₂O, 8.34%).

On heating there is partial melting and slight fuming owing to loss of P₂O₅ which accounts for the high loss on ignition. The crystals somewhat resemble those of CaH₄P₂O₈·H₂O and CaHPO₄·2H₂O. The two mixtures had been prepared by boiling syrupy phosphoric acid in a silica flask until the desired boiling point was reached, whereupon CaH₄P₂O₈·H₂O was added till present in small excess. A reflux condenser was then attached and boiling continued for 12 hr. The CaH₂P₂O₇ separated as well-formed small crystals after considerable supersaturation had occurred. This seems to be the first preparation of well-crystallised CaH₂P₂O₇, though a specimen with very little amorphous material has been obtained by thermal decomposition of CaH₄P₂O₈.⁸

The Space Model of the System CaO–P₂O₅–H₂O. We can now make the following deductions.

(1) The ice field is in two portions; a major one, strongly curved, rises almost vertically from the freezing-point curve (0° to –100°) of phosphoric acid solutions in the P₂O₅–temperature plane. This part of the field leans over very slightly in the direction of higher temperature. There is also a very small part of the ice field rising from the CaO–temperature plane above freezing-point curve (0° to –0.116°) of Ca(OH)₂ solutions. These two parts of the ice field are linked by the ice–hydroxyapatite curve which appears to pass through almost zero concentrations of CaO and P₂O₅ in the vicinity of 0°.

(2) The other boundaries of the ice field are given by the fields of H₃P₂O₉ (very short); CaH₄P₂O₈·H₂O; CaHPO₄·2H₂O; Ca₃P₂O₈·xH₂O; Hydroxyapatite; and Ca(OH)₂. The last three are all very short.

(3) The fields of CaH₄P₂O₈·H₂O and of CaH₄P₂O₈ are concave in the CaO–P₂O₅ plane while the fields of CaHPO₄·2H₂O and of CaHPO₄ are slightly convex in this plane.

(4) The highest CaO concentrations occur along the boundary between the regions of mono- and di-calcium phosphate which forms a well marked ridge on the space model. The maximum concentration (6.1% of CaO) occurs at the ice–CaH₄P₂O₈·H₂O–CaHPO₄·2H₂O quintuple point. It falls off very slowly in the direction of higher temperature, the value 5.6% of CaO being reached at 152°. The P₂O₅ values along this ridge increase from 19.62% at –7.5° to 53.00% at 152°.

⁷ Bassett, J., 1917, **111**, 620.

⁸ Hill, Hendricks, Fox, and Cady, *Ind. Eng. Chem.*, 1947, **39**, 1667.

(5) The solubility of monocalcium phosphate falls off rapidly with increasing concentrations of phosphoric acid so that the fields of solid $\text{H}_8\text{P}_2\text{O}_9$ and H_3PO_4 have hardly any width. In the case of $\text{H}_8\text{P}_2\text{O}_9$ the CaO content along the $\text{H}_8\text{P}_2\text{O}_9$ - $\text{CaH}_4\text{P}_2\text{O}_8$, H_2O curve reaches to just over 0.2% but along the H_3PO_4 - $\text{CaH}_4\text{P}_2\text{O}_8$ curve it amounts to a mere trace.

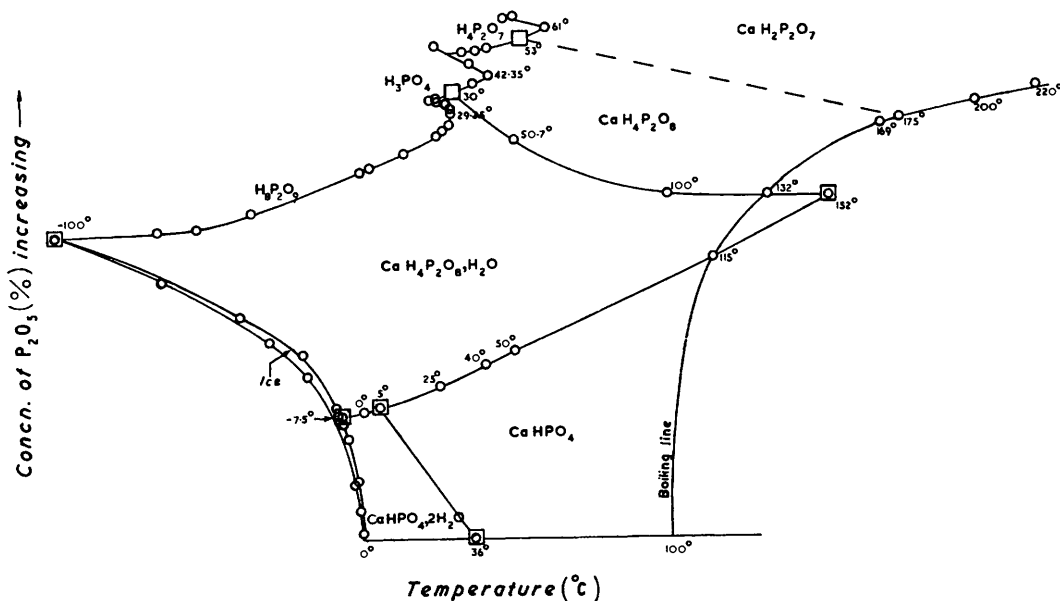
(6) The quintuple point with solid phases H_3PO_4 , $\text{CaH}_4\text{P}_2\text{O}_8$, and $\text{CaH}_4\text{P}_2\text{O}_8$, H_2O is probably at 30° and not at 39° as originally indicated.

(7) It is suggested that the boundary between the fields of $\text{CaH}_4\text{P}_2\text{O}_8$ and $\text{CaH}_2\text{P}_2\text{O}_7$ runs from a point at about 175° on the boiling line to a point at about 53° on the solubility curve of $\text{H}_4\text{P}_2\text{O}_7$.

(8) It is still uncertain whether tricalcium phosphate occurs in the CaO - P_2O_5 - H_2O system⁹ but, as the 1917 experiments⁷ seemed to show that it did, we still consider it to be one of the compounds which occur at low concentrations of CaO and P_2O_5 . The case of tetracalcium phosphate is, however, different and there seems to be no real evidence for its occurrence in, at any rate, aqueous calcium phosphate systems.*

(9) It is not easy to determine the exact temperature of quintuple points, especially those at low temperatures, owing to the slowness of the reactions involved. It has been suggested¹⁰ that the one at 36° (solid phases CaHPO_4 , H_2O , CaHPO_4 , and probably $\text{Ca}_3\text{P}_2\text{O}_8$, $x\text{H}_2\text{O}$) may occur at a rather higher temperature, which may be 40° . The

Space model of the system CaO - P_2O_5 - H_2O projected upon the temperature- P_2O_5 plane (to scale).



dilatometer is not very satisfactory, but a definite though slow expansion could be measured at as low a temperature as 36.4° .¹ The temperature 36° would only apply to the three-component system and the use of salt solutions to test the matter as in Lugg's work does not seem justified since the presence of other components could cause profound changes.

* [Added in Proof, 21.6.58.]—In an important recent paper on calcium orthophosphates Niels Bjerrum (*Kgl. danske Videnskab. Selskab. Mat.-fys. Medd.*, 1958, **31**, No. 7, 1—79) considers very fully the difficult problem of tricalcium phosphate and hydroxyapatite. It appears that anhydrous $\text{Ca}_3\text{P}_2\text{O}_8$, first obtained from high temperature fusions by Trömel (*Mitt. Kaiser Wilh. Inst. Eisenforsch.*, 1932, **14**, Abh. 198), has since been found in the low-temperature β -form as "stones" from the bladder and other parts of the human body. β - $\text{Ca}_3\text{P}_2\text{O}_8$ has also been found as a mineral, Whitlockite, by Frondel (*Amer. Mineralog.*, 1941, **26**, 145; 1943, **28**, 215).

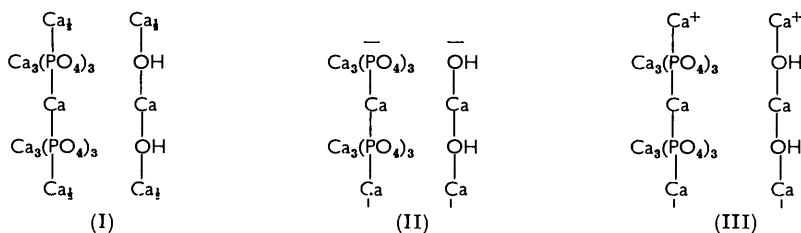
⁹ D'Ans and Knütter, *Angew. Chem.*, 1953, **65**, 578.

¹⁰ Lugg, *Trans. Faraday Soc.*, 1931, **27**, 297.

At present therefore this quintuple point is considered to be at 36° (with CaO, 0.0514%; P_2O_5 , 0.140%) though it may be somewhat lower, not higher.

(10) It seems likely that 21° as determined in 1908¹ is considerably too high for the quintuple point at which the three solid phases are $CaH_4P_2O_8 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$, and $CaHPO_4$. The much lower temperature makes the dilatometer even more unsatisfactory. With continuous shaking a suitable mixture of $CaH_4P_2O_8 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$, and solution will change completely to one of $CaH_4P_2O_8 \cdot H_2O$, $CaHPO_4$, and solution during several days at 25° , whereas much longer is required at 0° for the corresponding change in which $CaHPO_4$ is converted into $CaHPO_4 \cdot 2H_2O$. At 15° the mixture containing $CaHPO_4$ was also more stable than that containing $CaHPO_4 \cdot 2H_2O$ while the temperature of equal stabilities was at 5° as nearly as could be determined. We thus consider 5° to be correct for this quintuple point (with CaO, 5.98%; P_2O_5 , 21.00%). The region of $CaHPO_4 \cdot 2H_2O$ on the space model will have only about three-quarters of the area shown on the diagram of 1908.

(11) Arnold¹¹ has thrown much light upon the hydroxyapatite problem. He points out that the unit cell of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] can be represented most simply by (I). For an exposed surface the position may be represented by (II) or (III) according to whether the surface column Ca is absent or present; the latter is the most likely in neutral or alkaline solutions when the positive charges would be neutralised by hydroxyl ions.



If the surface hydroxyl groups are held up to about 1230° , as is likely since they are more than 5 \AA apart, the total constitutional water content corresponding to an average thickness of 13 "apatite" unit cells would be 2.06% as compared with the 1.79% calculated for the formula $Ca_{10}(PO_4)_6(OH)_2$. Arnold found that some of his preparations lost 2.07% of water above 1230° . This is also close to the deficit in analyses of precipitated hydroxyapatite solids reported by Bassett.⁷ Such finely divided solids would also carry much "adsorbed" water in addition to that present as hydroxyl ions on the exposed calcium ions. This is lost partly over sulphuric acid and partly on ordinary strong ignition. The smaller the number of apatite unit cells in the particles of a hydroxyapatite precipitate the more its composition will differ from that required by the formula $Ca_{10}(PO_4)_6(OH)_2$.

Preparations with a wide range of unit-cell thicknesses have been obtained, all of which give X-ray diagrams remarkably similar to that given by large crystals of apatite.¹¹

(12) It is impossible to show the basic region of the $CaO-P_2O_5-H_2O$ system to scale on the same diagram as the rest of the system. The areas and concentrations involved are so small that the whole basic region would only appear on the space model as a very low sharp edge rising vertically above the temperature- P_2O_5 plane along the axis of temperature. The maximum height of this would occur at -0.116° with 0.130% of CaO at the cryohydric point for coarse crystals of $Ca(OH)_2$.⁷

The solubility of $Ca(OH)_2$ falls off rapidly with increasing temperature and is 0.0523% of CaO at 99° and 0.0246% of CaO at 150° .¹² The above-mentioned sharp edge would subside in the same way. It is difficult to say just what effect this would have on the areas of hydroxyapatite and $Ca_3P_2O_8 \cdot xH_2O$. Their "alkaline" region would be greatly

¹¹ Arnold, *Trans. Faraday Soc.*, 1950, **46**, 1061.

¹² Shenstone and Cundall, *J.*, 1888, **53**, 550.

restricted but owing to increased hydrolysis at higher temperatures they would probably spread into regions of higher $P_2O_5:CaO$ ratios, as happens to $CaHPO_4 \cdot 2H_2O$ and $CaHPO_4$.

(13) The diagram presented is true to scale and is a projection of the space model of the system $CaO-P_2O_5-H_2O$ upon the temperature- P_2O_5 plane. Squares indicate quintuple points. It is not considered necessary to give a sketch of the solid model which is really very simple. It can be regarded as a double wedge sloping downwards from a central ridge in two directions. There is a convex slope in the direction of decreasing P_2O_5 and a concave slope in the direction of increasing P_2O_5 . There is in addition a third general downward slope in the direction of increasing temperature and away from the almost vertical ice field.

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[Received, March 19th, 1958.]
