

### XCIV.—*Electrometric Study of the Precipitation of Phosphates.*

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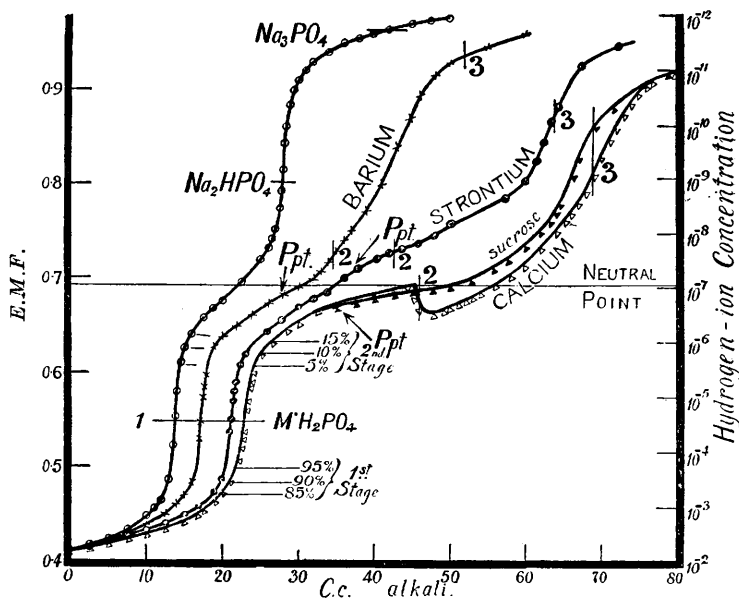
AN attempt is made in this paper to correlate the dissociation of phosphoric acid with the precipitation reactions in which it is involved. Phosphoric acid behaves in its first stage of ionisation as a strong acid,  $K_1 = 9.4 \times 10^{-3}$ , in its second as a weak acid,  $K_2 = 1.4 \times 10^{-7}$ , and in its third stage as an extremely weak acid,  $K_3 = 2.7 \times 10^{-12}$ , so weak that its dissociation can only just be determined. It appears probable, from the very low order of magnitude of  $K_3$ , that the third hydrogen atom of phosphoric acid might be incapable of reacting with the majority of weak bases unless the phosphates happen to be very insoluble and the phosphate-ion concentrations of the mother-liquors are kept sufficiently large to exceed the solubility products without permitting the hydrogen-ion concentrations to become so small as to cause precipitation of the hydroxides. Hence, in order to study the part played by phosphoric acid in the various precipitation reactions, the hydrogen-ion concentrations which prevail throughout their courses have been measured by means of the hydrogen electrode. Two series of potentiometric titrations with the hydrogen and normal calomel electrodes have been made in the manner outlined in previous communications (J., 1924, **125**, 1572; 1925, **127**, 2110): the first comprises the reactions between solutions of phosphoric acid and strong bases, *viz.*, the hydroxides of sodium, calcium, barium, and strontium; and the second series deals with the action of trisodium phosphate, chosen because it involves the third stage of ionisation, on solutions of salts of typical metallic bases. A titration by lime water of phosphoric acid in a solution of sucrose was included in the first series in view of the discordant observations of Wendt and Clarke (*J. Amer. Chem. Soc.*, 1923, **45**, 881) and Hoffman and Gortner

(*J. Physical Chem.*, 1925, **29**, 769). [See also Holt, LaMer, and Chown (*J. Biol. Chem.*, 1925, **64**, 509) and Farnell (*J. Soc. Chem. Ind.*, 1926, **45**, 343T).]

## Series I.

Fig. 1 gives the hydrogen-electrode titration curves at 20° of (1) 100 c.c. of 0.01277*M*-H<sub>3</sub>PO<sub>4</sub> with 0.0919*N*-NaOH, (2) 100 c.c. of 0.00965*M*-H<sub>3</sub>PO<sub>4</sub> with 0.0558*N*-Ba(OH)<sub>2</sub>, (3) 100 c.c. of 0.00765*M*-H<sub>3</sub>PO<sub>4</sub> with 0.0359*N*-Sr(OH)<sub>2</sub>, (4) 100 c.c. of 0.01024*M*-H<sub>3</sub>PO<sub>4</sub> with 0.0447*N*-Ca(OH)<sub>2</sub>, and (5) 100 c.c. of 0.01024*M*-H<sub>3</sub>PO<sub>4</sub>

FIG. 1.



containing 5 g. of sucrose with 0.0447*N*-Ca(OH)<sub>2</sub>. With the exception of the sodium hydroxide titration and the alkaline-earth titrations up to the addition of the first equivalent, the *E.M.F.*'s recorded were not true equilibrium values, but were those indicated immediately after each addition of the reactant, for, as Wendt and Clarke observed in their lime-water titrations, the initial *P.D.*'s become smaller when the solutions stand for some time, through the slow reactions which take place between the precipitate and the added alkaline earth.

It is necessary to consider the three dissociation constants of phosphoric acid which have been found to satisfy the sodium hydroxide titration curve, especially in view of the different values

of  $K_3$  which have been reported. Thus Abbott and Bray (*J. Amer. Chem. Soc.*, 1909, **31**, 729) gave  $K_3$  at  $18^\circ$  as  $3.6 \times 10^{-13}$ , whereas Prideaux and Ward (*J.*, 1924, **125**, 423) have recently shown that their  $p_H$  measurements and those of other workers give values ranging from 1.54 to  $5.3 \times 10^{-12}$ . Excluding the small portions of the curve about the points of inflexion, the hydrogen-ion concentrations corresponding to the first two sections of the curve are due (see Britton, *J.*, 1925, **127**, 1896) entirely to the equilibria governed by  $K_1 = [H^+][H_2PO_4']/[H_3PO_4]$  and  $K_2 = [H^+][HPO_4'']/[H_2PO_4']$ , and consequently the simple method adopted in calculating the dissociation constants of malonic acid is applicable. The large hydroxyl-ion concentrations produced during the neutralisation of disodium phosphate with sodium hydroxide are due to a portion of the added alkali taking part in the hydrolysis—in effect remaining unattacked. The concentration of this unattacked alkali may be found directly from the *E.M.F.*'s, assuming the complete ionisation of the solutes, and therefore the concentration of sodium phosphate actually formed is the difference between this and the concentration which would have been produced if all the added alkali had formed trisodium phosphate. The method of calculating  $K_3$  is identical with that previously used to find the dissociation constant of dextrose. Table I gives the *E.M.F.*'s of the hydrogen electrode, compared with the normal calomel electrode, for the titration of phosphoric acid with sodium hydroxide, together with the various calculated ionic concentrations and the dissociation constants to which they lead.

The values of the dissociation constants given in the last column show that the values  $K_1 = 9.4 \times 10^{-3}$ ,  $K_2 = 1.4 \times 10^{-7}$ , and  $K_3 = 2.7 \times 10^{-12}$  reproduce fairly well the three sections of the titration curve. The values of  $K_1$  and  $K_2$  are slightly lower than Abbott and Bray's (*viz.*,  $K_1 = 1.1 \times 10^{-2}$ ,  $K_2 = 1.95 \times 10^{-7}$ ), whereas that of  $K_3$  is seven times greater than their value. It is, however, in agreement with the recent value of Prideaux.

On comparing the alkaline-earth titration curves, up to the points corresponding to the beginning of precipitation, with that of sodium hydroxide, it will be seen that they cover almost identical ranges of hydrogen-ion concentration. In the lime-water titration precipitation was delayed until 1.53 equivs. (= 35 c.c.) had been added and  $p_H$  6.72 was attained. On standing over-night, a solution of the same concentrations deposited an appreciable amount of precipitate and its  $p_H$  fell to 5.98; in fact, precipitates were formed when solutions were allowed to stand which contained only just over 1 equiv. of calcium hydroxide. The delay in precipitation and the high initial  $p_H$  were caused by neutralisation taking place

TABLE I.

Titration of 100 c.c. of 0.01277*M*-H<sub>3</sub>PO<sub>4</sub> with 0.0919*N*-NaOH at 20°(NaH<sub>2</sub>PO<sub>4</sub> = 13.9 c.c.; Na<sub>2</sub>HPO<sub>4</sub> = 27.8 c.c.)

NaOH (c.c.).	<i>E.M.F.</i>	<i>p</i> <sub>H</sub> .	[H <sub>2</sub> PO <sub>4</sub> ' ] × 10 <sup>3</sup> .	[H <sub>3</sub> PO <sub>4</sub> ] × 10 <sup>3</sup> .	<i>K</i> <sub>1</sub> × 10 <sup>3</sup>
0.0	0.408	2.14	7.24	5.53	9.55
2.55	0.416	2.28	7.54	4.92	8.13
5.0	0.423	2.40	8.36	3.80	8.71
7.5	0.433	2.57	9.10	2.78	8.91
10.0	0.447	2.81	9.90	1.71	9.12
11.0	0.455	2.94	10.26	1.24	9.55
12.0	0.464	3.10	10.64	0.76	11.22
13.0	0.486	3.48	10.90	0.36	10.00
13.5	0.521	4.10	11.00	0.26	3.31

Mean 9.4

NaOH (c.c.).	<i>E.M.F.</i>	<i>p</i> <sub>H</sub> .	C.c. NaH <sub>2</sub> PO <sub>4</sub> .	C.c. Na <sub>2</sub> HPO <sub>4</sub> .	<i>K</i> <sub>2</sub> × 10 <sup>7</sup> .
14.5	0.610	5.60	13.3	0.6	1.12
15.0	0.625	5.86	12.8	1.1	1.18
16.0	0.640	6.11	11.8	2.1	1.38
17.5	0.657	6.40	10.3	3.6	1.38
20.0	0.675	6.71	7.8	6.1	1.51
22.5	0.695	7.06	5.3	8.6	1.41
25.0	0.719	7.47	2.8	11.1	1.35
26.0	0.731	7.67	1.8	12.1	1.44
27.0	0.751	8.01	0.8	13.1	1.35
27.5	0.773	8.39	0.3	13.6	1.82

Mean 1.4

NaOH (c.c.).	<i>E.M.F.</i>	<i>p</i> <sub>H</sub> .	[PO <sub>4</sub> '''] × 10 <sup>3</sup> .	[HPO <sub>4</sub> '''] × 10 <sup>3</sup> .	<i>K</i> <sub>3</sub> × 10 <sup>12</sup> .
29.0	0.883	10.28	0.66	9.24	3.72
30.0	0.909	10.72	1.02	8.80	2.24
31.0	0.921	10.92	1.42	8.33	2.04
32.0	0.928	11.05	1.80	7.87	2.04
34.0	0.940	11.26	2.43	7.10	1.91
36.0	0.949	11.40	3.03	6.36	1.91
38.0	0.954	11.49	3.70	5.55	2.19
40.0	0.959	11.57	4.29	4.83	2.40
42.5	0.964	11.66	4.91	4.05	2.63
45.0	0.968	11.72	5.65	3.16	3.39
47.5	0.973	11.81	5.81	2.85	3.16
50.0	0.975	11.85	6.52	1.99	4.57

Mean 2.7

immediately, whereas the precipitation from the supersaturated solution was a matter of time. Had neutralisation only taken place, the hydrogen-ion concentration would have been equal to  $[\text{H}_2\text{PO}_4'] \times K_2/[\text{HPO}_4''] = (2 - n) \times 1.4 \times 10^{-7}/(n - 1)$ , where *n* is the number of eqivs. of alkaline earth, from which it follows that the *p*<sub>H</sub> of the calcium solution when on the point of precipitation should have been 6.91, which is slightly higher than the observed value, 6.72, the difference evidently being due to the precipitation reaction having proceeded to a small extent. The presence of sucrose in the phosphoric acid solution did not impede precipitation. In the baryta titration, 1.62 eqivs. were required to start precipitation, which took place at *p*<sub>H</sub> 6.88; on standing over-night further

precipitation occurred and the  $p_H$  of the solution fell to 6.07. Strontium hydroxide solution produced a precipitate with 1.78 equivs. (38 c.c.); the  $p_H$  was then 7.34, but it became 6.60 after standing over-night, more precipitate having separated. These titrations up to the point of precipitation consisted chiefly of neutralisation, for by calculation it is found that for neutralisation alone the  $p_H$  should have been 7.07 in the barium titration instead of 6.88 observed, and 7.40 in the strontium titration instead of 7.34.

The precipitates first formed were the monohydrogen phosphates,  $M'HPO_4$ , which by the addition of more alkaline earth became converted into the normal phosphates,  $M_3(PO_4)_2$ . The inflexion in the baryta-titration curve occurred during the addition of the third equiv., and therefore the precipitate was a mixture of di- and tri-barium phosphates, whereas in the strontia curve the inflexion was not produced until the third equiv. had been added, showing that the precipitate was the normal strontium phosphate. The final inflexion in the calcium hydroxide titration occurred when the third equiv. had been added, suggesting that at that stage the precipitate was tricalcium phosphate. It will, however, be observed that further additions of lime water did not cause as great an increase in  $p_H$  as in the other titrations. This was due to the absorption by the calcium phosphate of some calcium hydroxide thus rendering the phosphate basic. Bassett (J., 1917, 114, 620) found that one molecule of tricalcium phosphate can absorb one-third of a molecule of calcium hydroxide to form "hydroxyapatite,"  $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ ; he believes that this is the calcium phosphate which can permanently exist in the soil under ordinary conditions.

The variation in hydrogen-ion concentration, which occurred in the lime-water reaction just after two equivs. had been added, is remarkable in that the addition of more reactant actually caused an increase in the concentration of hydrogen ions. Wendt and Clarke (*loc. cit.*) found a similar change, but theirs occurred while the second equiv. was being added, doubtless owing to longer times being allowed to elapse before making measurements. An examination of the  $p_H$  data corresponding to the addition of the second equiv. of calcium hydroxide in the present titration reveals that the high  $p_H$  values were such as would be produced by a large concentration of  $HPO_4''$  ions, caused through supersaturation, as compared with that of  $H_2PO_4'$  ions. Assuming that in the first place only the dicalcium phosphate was being formed and partly precipitated, it appears that, when the second equiv. of lime water had been added, the concentration of monocalcium phosphate, and therefore of  $H_2PO_4'$  ions, had been reduced to a minimum, the little remaining being produced by the hydrolysis of the precipitate. A sudden diminution

in the concentration of  $\text{HPO}_4''$  ions would lead to a sudden increase in  $p_{\text{H}}$ . Actually a sudden decrease in  $p_{\text{H}}$  was obtained and this was accompanied by further precipitation. It appears probable therefore that the added calcium hydroxide reacted with the dicalcium phosphate remaining in solution, causing precipitation of the tricalcium salt, and in so doing it also decomposed the supersaturated solution, precipitating some dicalcium salt and possibly a little of the normal salt in accordance with the equation suggested by Wendt and Clarke :  $4\text{CaHPO}_4 = \text{Ca}_3(\text{PO}_4)_2 + \text{Ca}(\text{H}_2\text{PO}_4)_2$ . The  $p_{\text{H}}$  data calculated from the phase-rule data of Bassett (*vide infra*) show that both the di- and the tri-calcium phosphates attain equilibrium with liquid phases whose  $p_{\text{H}}$ 's are about 5.5 through equilibria involving  $\text{H}_2\text{PO}_4'$  and  $\text{HPO}_4''$  ions, the former being in considerable excess. It would be expected, therefore, that a  $p_{\text{H}}$  of 5.5 would represent the lowest value to which this downward inflexion could attain, and it is interesting to find that this is about the value shown by Wendt and Clarke's curve. The higher  $p_{\text{H}}$  obtained by the author is due to insufficient time being allowed for the attainment of final equilibrium. The earlier appearance of the inflexion in Wendt and Clarke's curve was due to the precipitation of the two phosphates of calcium.

Since this work was completed, Holt, LaMer, and Chown (*loc. cit.*), and Farnell (*loc. cit.*) have described similar increases in hydrogen-ion concentration, whereas Hoffman and Gortner (*loc. cit.*), using a solution of calcium succrate in order to obtain a calcium solution more concentrated than saturated lime water, found no such variation. They considered that the quantity of sucrose present in their work was such as to be without effect on the hydrogen-ion concentrations. The titration curve of phosphoric acid in presence of sucrose given in Fig. 1 shows that sucrose acts as a buffer in preventing an increase in hydrogen-ion concentration. Wendt and Clarke found, by allowing 10 days for the attainment of equilibrium, that the curve became rectilinear during the addition of the greater part of the second and third equivs. of calcium hydroxide, and indicated hydrogen-ion concentrations varying from  $p_{\text{H}}$  5.5, when a little more than the first equiv. had been added, to  $p_{\text{H}}$  6.0 at 2.5 equivs. This is as would be expected from a consideration of Bassett's work (*vide infra*). Farnell obtained similar results by boiling the solutions and cooling to  $20^\circ$  before measuring the  $p_{\text{H}}$ . By allowing the solutions to stand over-night in stoppered bottles, the author found that the change in hydrogen-ion concentration was gradual and varied from  $p_{\text{H}}$  5.98 at 1.53 equivs. to  $p_{\text{H}}$  6.52 at 2.5 equivs. These precipitations had not, however, become complete.

The considerable amount of supersaturation, with its consequent effect on the hydrogen-ion concentration, which occurs when alkaline

earths are added to phosphoric acid solutions, renders it difficult to ascertain, by a titration method, when a precipitate should begin to separate. The  $p_H$  at which calcium begins to separate as a phosphate is of some importance in the chemistry of soils, and therefore certain data relating to the ternary system  $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  obtained by Bassett (J., 1917, 111, 624; *Z. anorg. Chem.*, 1908, 59, 1) at 25° and by Cameron and Bell (*J. Amer. Chem. Soc.*, 1905, 27, 1512) have been studied with respect to the stage of neutralisation of the phosphoric acid in the liquid phases; then, either by comparison with the neutralisation curve (Fig. 1), or by calculation,\* an approximate estimate has been made of the hydrogen-ion concentrations of the liquid phases in equilibrium with solid phases containing varying amounts of phosphate. Table II was compiled from Bassett's data, the product  $[\text{Ca}^{2+}][\text{HPO}_4^{2-}]$  having been calculated on the assumption that both the mono- and the di-calcium phosphate in solution were completely ionised, an assumption which probably only holds for the very dilute solutions, but which, nevertheless, permits of a satisfactory computation for other solutions. The ionic products  $[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$  are approximate and were calculated from the hydrogen-ion concentrations, the concentration of  $\text{HPO}_4^{2-}$  ions, and  $K_3 = 2.7 \times 10^{-12}$ .

It will be seen from the table that those liquid phases which contained 0.149%  $\text{P}_2\text{O}_5$  ( $= 0.02M\text{-H}_3\text{PO}_4$ ) or less, as a rule contained calcium hydroxide sufficient to neutralise about 5% of the second stage, giving hydrogen-ion concentrations of the order of  $10^{-5.5}$ . The amount of lime became in excess of 2 equivs. for liquid phases containing less than 0.00613%  $\text{P}_2\text{O}_5$  ( $= 0.0009M\text{-H}_3\text{PO}_4$ ). The solid phases which were more basic than  $\text{CaHPO}_4$  are indicated by the molar ratio  $\text{PO}_4/\text{CaO}$ , which is 0.67 for tricalcium phosphate and 0.60 for the substance, hydroxyapatite,  $3\text{Ca}_3(\text{PO}_4)_2\text{Ca}(\text{OH})_2$ . The values of the ratio suggest that the solid phases in equilibrium with the most dilute liquid phases were hydroxyapatite, whereas the ratios corresponding to the more concentrated liquid phases fall, with one exception, between 0.66 and 0.95, proving that the solid phases were either mixtures of tri- and di-calcium phosphate, or possibly dicalcium phosphate in various stages of decomposition. The presence of two solid phases *in equilibrium* with variable liquid phases is incompatible with the phase rule, and it is considered that the conversion of di-calcium phosphate into the normal salt is very slow owing to the ionic requirements of the one being set up simultaneously with those of the other. Consequently, the solid phases may have been indefinite

\* The calculation was based on  $[\text{H}^+] = (100 - x) \times 1.4 \times 10^{-7}/x$ , where  $x$  = the % of neutralisation of the second stage,  $K_2$  being assumed to be the same at 25° as at 20°.

TABLE II.

*Analysis of Bassett's data of the system CaO-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O.*

%CaO.	%P <sub>2</sub> O <sub>5</sub> .	Solid phase.	% Neutralised.*	p <sub>H</sub> .	[Ca <sup>++</sup> ][HPO <sub>4</sub> <sup>-</sup> ] × 10 <sup>6</sup> .	[Ca <sup>++</sup> ] <sup>2</sup> [PO <sub>4</sub> <sup>3-</sup> ] <sup>2</sup> × 10 <sup>25</sup> .
1.181	3.613	CaHPO <sub>4</sub> .	83 (I)	3 approx.	—	—
0.826	2.387	„	81 (I)	3 „	—	—
0.165	0.417	{ CaHPO <sub>4</sub> and CaHPO <sub>4</sub> ·2H <sub>2</sub> O. }	0.04 (II)	—	5.9	—
0.0696	0.178	CaHPO <sub>4</sub> ·2H <sub>2</sub> O.	99.6 (I)	—	—	—
0.0617	0.149	„	5.1 (II)	5.6	11.7	13
0.0507	0.121	„	6.3 (II)	5.7	9.7	16
0.0485	0.119	„	3.3 (II)	5.4	4.9	1.0
0.0427	0.105	„	3.1 (II)	5.4	3.5	0.4
		PO <sub>4</sub> /CaO in solid phase.				
0.0406	0.0980	0.76	5.1 (II)	5.6	5.1	2.0
0.0389	0.0947	0.79	4.1 (II)	5.5	3.8	0.8
0.0373	0.0897	0.95	5.5 (II)	5.6	4.6	1.6
0.0326	0.0777	0.62	6.4 (II)	5.7	4.1	1.6
0.0299	0.0727	0.67	4.4 (II)	5.5	2.4	0.2
0.0269	0.0607	0.66	12.4 (II)	6.0	5.1	7.9
0.0191	0.0465	0.70	4.1 (II)	5.5	0.9	0.02
0.0175	0.0423	0.71	4.9 (II)	5.6	0.9	0.05
0.0174	0.0414	0.69	6.5 (II)	5.7	1.2	0.08
0.0167	0.0405	0.69	4.6 (II)	5.5	0.8	0.01
0.0126	0.0332	—	96 (I)	—	—	—
0.0122	0.0302	0.66	2.4 (II)	5.2	0.2	0.0003
0.00893	0.0196	0.63	12.0 (II)	6.0	0.4	0.03
0.00582	0.0134	0.62	10.1 (II)	5.9	0.2	0.002
0.00600	0.00613	0.62	4.9 (III)	11 approx.	—	—

\* The Roman numerals (I), (II), and (III) relate to the first, second, and third stages, respectively.

and unstable mixtures, although it appeared, as far as could be ascertained experimentally, that equilibrium had been established. The foregoing explanation appears to be valid, for if the solubility product of dicalcium phosphate be assumed to be  $5 \times 10^{-6}$  (approx.), and that of the tricalcium salts to be about  $1 \times 10^{-25}$ , then it is evident from the table that for many liquid phases the two stipulated conditions prevailed at the same time. The decrease in the ionic product of the tricalcium salt (shown by the last few values in the last column) to less than the probable value of the solubility product,  $1 \times 10^{-25}$ , may have been due to the formation of a basic phosphate.

The p<sub>H</sub> data given in Table II are of interest on account of their bearing on the reactions which take place in soils when treated with phosphatic fertilisers. If the p<sub>H</sub> of the "soil solution" falls below 5.5, the calcium phosphate in the soil will pass into the soluble state, though when in this condition there will be a great tendency for some of the phosphate to suffer "reversion" through reaction with colloidal alumina, but when lime is added so as to raise the p<sub>H</sub> to 5.5 and above, the phosphate begins to become insoluble, initially as the dicalcium salt, and finally as the basic phosphate. It would appear



that these changes in the composition of the insoluble calcium phosphate can take place without any great diminution in the acidity of the soil. The  $p_H$ , 5.9, attained when the  $PO_4/CaO$  ratio in the solid phases had become 0.62, confirms Bassett's observation that hydroxyapatite can exist in faintly acid as well as in neutral or alkaline solutions, and that it can probably exist permanently in soils under ordinary conditions, for any di- or tri-calcium phosphate which may first be formed will ultimately become decomposed.

Soil solutions in equilibrium with the dicalcium phosphate contain relatively large amounts of partly neutralised phosphoric acid which, when removed either by "reversion," by the plant, or by drainage, will cause the solid phases to decompose and eventually to become basic without any great change in  $p_H$  taking place. The conversion of the phosphate into the insoluble basic state renders it unavailable to the plant. Thus Gedroiz (*Zhur. Opit. Agron.*, 1911, 12, 529) found that tricalcium phosphate gave the best immediate results on soils not saturated with bases. The necessity of having the soil just on the acidic side of neutrality has recently been emphasised by von Wrangell (*Landw. Vers.-Stat.*, 1920, 96, 1), who recommends the use of "physiologically acid fertilisers," such as ammonium sulphate, to render any phosphate available.

### Series II.

The variation in hydrogen-ion concentration which occurred at 20° when a  $N/10$ -solution of trisodium phosphate was added to 100 c.c. of the salt solutions (Table III) was followed electrometrically. The *E.M.F.*'s were reproducible, except in the final stages of the chromium and magnesium titrations. Table III also contains the  $p_H$ 's at which the phosphate precipitates began to separate, and, for purposes of comparison, the respective hydroxide  $p_H$ 's.

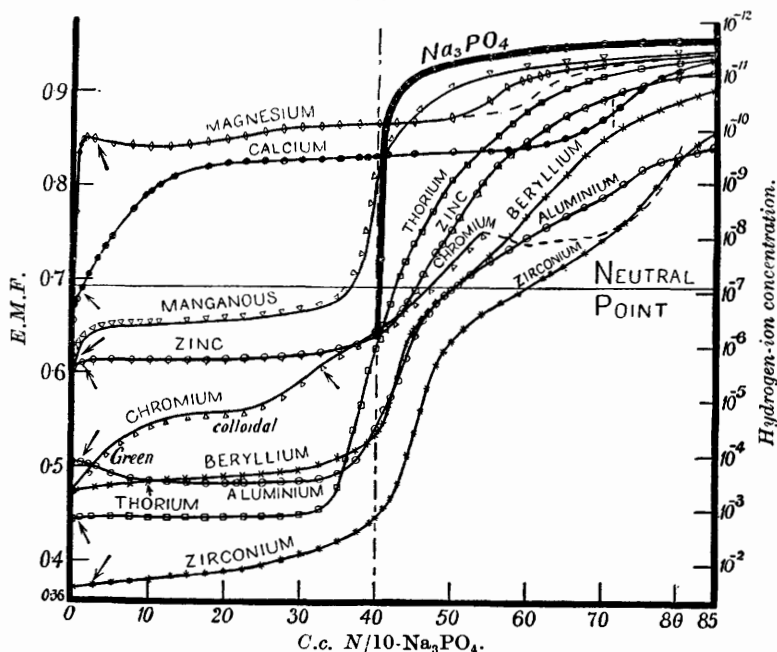
TABLE III.

Solution titrated.	Phosphate $p_H$ .	Hydroxide $p_H$ .
0.02M·MgSO <sub>4</sub> .....	9.76	10.49
0.0358M·CaCl <sub>2</sub> .....	7.00	—
0.02M·MnCl <sub>2</sub> .....	5.76	8.43
0.02M·ZnSO <sub>4</sub> .....	5.66	5.20
0.00667M·Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ,K <sub>2</sub> SO <sub>4</sub> .....	{ 4.62 5.65 }	5.34
0.00667M·Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .....	3.79	4.14
0.02M·BeSO <sub>4</sub> .....	3.41	5.69
0.01M·ThCl <sub>4</sub> .....	2.72	3.51
0.01M·ZrCl <sub>4</sub> .....	1.57	1.86

The curves showing the hydrogen-ion concentrations acquired when increasing amounts of trisodium phosphate had been added are given in Fig. 2. The amount of trisodium phosphate required

to form the normal metallic phosphate was 40 c.c. in every case except that of calcium chloride, in which it was 71.6 c.c. The curve marked  $\text{Na}_3\text{PO}_4$  was obtained by adding  $N/10$ -sodium phosphate solution to 140 c.c. of solution (*i.e.*, the volume attained in the precipitation reactions when stoichiometrical amounts of the phosphate solution had been added) containing an amount of sodium chloride equal to the amount of neutral salt formed in the precipitation reactions with 40 c.c. of sodium phosphate. It would therefore represent the variation in hydrogen-ion concentration on

FIG. 2.



adding an excess of the reactant, if the pure normal phosphates had been precipitated, leaving in solution amounts of phosphate so small as to exert no "buffer action." The arrows denote the beginning of precipitation.

In no instance did the curve corresponding to an excess of the reactant coincide with this curve, the two nearest being those of manganese and calcium. The others are widely divergent. The  $p_{\text{H}}$  data given in Table III show that the phosphate precipitates, with the exception of that of zinc, separated from solutions whose hydrogen-ion concentrations were greater than those requisite for the precipitation of the corresponding hydroxides; and thus it

appears that, whilst it may be possible to obtain the normal phosphates by the use of an amount of trisodium phosphate insufficient to give complete precipitation, yet as soon as sufficient reactant has been added to bring the  $p_H$  of the solution to that necessary for the precipitation of the hydroxide, any metallic salt remaining in solution will then be precipitated, and, moreover, there will be a strong tendency for the precipitate to be decomposed. That some such reaction must have taken place is evident from the curves. The depression of the manganese and the calcium curves must have been caused by the "buffer action" of the added sodium phosphate on the  $HPO_4''$  ions, which had been supplied to the solutions by the precipitates. The greater hydrogen-ion concentrations set up in the zinc, beryllium, aluminium, and thorium reactions were, as may be seen from the sodium hydroxide curve in Fig. 1, of the same magnitude as those produced in the second, and subsequently the third, stage of neutralisation. Hence the precipitates must have decomposed to furnish the mother-liquor with  $H_2PO_4'$  ions, some of which, by reacting with the added phosphate, became converted into  $HPO_4''$  ions.

No inflexion occurred in the zirconium chloride reaction when the stoicheiometrical quantity of sodium phosphate had been added, though one appeared on the addition of a small excess. By comparing the range of hydrogen-ion concentrations produced during the addition of this excess with that obtained towards the end of the neutralisation of the first stage of phosphoric acid (Fig. 1), it will be seen that the equilibria which produce these relatively large concentrations of hydrogen ions involve some free phosphoric acid. This must have been liberated through the extreme weakness of zirconium hydroxide, with the result that a highly basic zirconium phosphate was precipitated, the formation of which might have been inferred from the fact that zirconium chloride solutions are very considerably hydrolysed. Thus it was found (Britton, J., 1925, 127, 2133) that a freshly prepared solution of the concentration used in this titration was hydrolysed to the extent of 54%, and consequently the free acid liberated an equivalent amount of phosphoric acid on reacting with trisodium phosphate. The middle point of the first inflexion (corresponding with the addition of 45 c.c., an excess of 5 c.c.) represents the stage when the liberated phosphoric acid had reacted with the added phosphate to form monosodium phosphate, in accordance with the equation  $Na_3PO_4 + 2H_3PO_4 = 3NaH_2PO_4$ , from which it follows that the excess of 5 c.c. reacted with twice the amount, *i.e.*, 10 c.c., of phosphoric acid. The total amount of phosphoric acid was equivalent to 40 c.c., and of this 13.3 c.c. corresponded to the first stage of dissociation. The

amount of phosphoric acid which had escaped precipitation was therefore 10/13.3 of the quantity required for the normal phosphate of zirconium, and hence the composition of the precipitate might be represented as  $6\text{ZrO}_2 \cdot \text{P}_2\text{O}_5$ . The curve obtained on adding a further excess of the reactant, instead of being sharply inflected through  $p_{\text{H}}$  9 owing to the complete formation of disodium phosphate, showed that a considerable "buffer action" occurred between  $p_{\text{H}}$  6 and 10. It appears, therefore, from the expression  $[\text{H}'] = K_2[\text{H}_2\text{PO}_4']/[\text{HPO}_4'']$  governing the hydrion concentrations during the second stage of neutralisation, that the precipitate itself, in being decomposed, must have exerted some buffering action by imparting to the mother-liquor a small but continuous concentration of  $\text{H}_2\text{PO}_4'$  ions.

The precipitation curve of aluminium phosphate is interesting in that the first addition of sodium phosphate caused an increase in the concentration of hydrogen ions, reaching a maximum at  $p_{\text{H}}$  3.43 with 17.5—20 c.c. The precipitate became very basic when an excess of sodium phosphate was added as shown by the comparatively large buffering effect—at 80 c.c. the  $p_{\text{H}}$  was 9.41; at 100 c.c., 10.02; at 120 c.c., 10.24; and at 140 c.c., 10.33. The hydrolysis of the precipitate into aluminium hydroxide was accompanied by its gradual dissolution in the sodium phosphate solution. Thus the solution became translucent with 80 c.c. and quite clear with 140 c.c. Reference to the hydrogen-ion concentration curve showing the action of alkali on aluminium sulphate solution (Britton, J., 1925, 127, 2121) shows that sodium aluminate began to form when the  $p_{\text{H}}$  became between 9 and 10. Hence it appears that the dissolution of the precipitate in an excess of sodium phosphate was due to the formation of sodium aluminate, the necessary free alkali being furnished by the trisodium phosphate through the exceptional weakness of phosphoric acid in its third stage of ionisation and the resulting hydrolysis of its sodium salt. The inability of disodium phosphate, when added in excess, to cause the precipitate to dissolve is due to the low  $p_{\text{H}}$  which it sets up. An excess of this precipitant reduces the hydrogen-ion concentration considerably below that at which aluminium hydroxide becomes precipitable, causing the precipitate to hydrolyse. Thus Munroe (*Amer. J. Sci.*, 1871, [iii], 1, 329) found that a precipitate,  $\text{AlPO}_4 \cdot \text{Al}(\text{OH})_3 \cdot 2.5\text{H}_2\text{O}$ , was obtained when an alum solution was treated with an excess of the disodium salt.

The ease with which aluminium phosphate becomes decomposed on decreasing the hydrogen-ion concentration, even though the reagent used may itself be a soluble phosphate, throws some light on the manner in which vegetation obtains its phosphorus from

the soil. When a soluble phosphatic fertiliser, such as superphosphate of lime, is added to a soil, and especially if the soil be sour, "reversion" of the phosphate occurs through the formation of insoluble phosphate on the surfaces of the colloidal particles of hydrated alumina and ferric oxide (see, *e.g.*, Lichtenwalner, Flenner, and Gordon, *Soil Sci.*, 1923, **15**, 157; Hall and Vogel, *ibid.*, p. 367). Marais (*ibid.*, 1922, **13**, 355), in a study of the application of aluminium phosphate as a fertiliser, concluded that, in spite of its low solubility in citric acid, it is of service in soils well stocked with lime, but should never be used on acid soils unless lime is applied in intimate contact with it. Slaked lime causes aluminium phosphate to decompose with the formation of soluble calcium phosphate until  $p_H$  5.5 is reached.

In the author's earlier papers, stress was laid on the remarkable property of beryllium and chromium in forming "soluble basic salts," and attempts have been made to trace any effects that this factor may have on the reactions of the salts of these metals. Precipitation of the basic chromate, carbonate, and borate did not occur until comparatively large amounts of precipitant had been added, and considerable changes in hydrogen-ion concentration had taken place (J., 1925, **127**, 2120: 1926, 125). Although precipitation did not take place from the beryllium sulphate solution until 7.5 c.c. of sodium phosphate had been added, the delay was not accompanied by any great change in hydrogen-ion concentration. As mentioned above, the beryllium precipitate was a basic phosphate. Bleyer and Müller (*Z. anorg. Chem.*, 1913, **79**, 263) assigned the formula  $\text{BeO}, 2\text{Be}_3(\text{PO}_4)_2, 13\text{H}_2\text{O}$  to a precipitate similarly obtained.

In the chromium sulphate titration, however, the effect was pronounced. At first the sodium phosphate merely caused the violet solution to turn green—a point of importance in connexion with the question of the colours of chromium salt solutions, and one which has always been observed whenever a violet chromium salt solution has been rendered basic (*loc. cit.*). Simultaneously an appreciable decrease in hydrogen-ion concentration occurred until 12 c.c. (= 0.90 equiv. per atom of Cr) had been added,  $p_H = 4.62$ , a cloudiness then being observed. For the next 10 c.c. the  $p_H$  remained nearly constant, although the solution became more and more colloidal, and thereafter a steady rise in  $p_H$  occurred, coagulation taking place at  $p_H$  5.65 with 32.5 c.c. (= 2.44 equivs.). The bulk of the precipitate was green and flocculent, but it contained a small quantity of a violet crystalline precipitate, apparently the normal chromium phosphate. The delay in precipitation is significant, as also is the fact that when it took place the hydrogen-ion concentration of the mother-liquor was not very far from that

at which chromium hydroxide is precipitated, *viz.*,  $p_H$  5.3. The diminution in hydrogen-ion concentration was gradual until 54 c.c. (= 4.05 equivs.) of sodium phosphate had been added,  $p_H = 8.07$ , at which stage the *E.M.F.*'s not only became very unsteady, but also showed a remarkable increase in hydrogen-ion concentration. The changes which took place immediately after the addition of each new amount of sodium phosphate are shown by the broken line. The hydrogen-ion concentration subsequently grew smaller, such that when 80 c.c. had been added the  $p_H$  had become 9.71. Precipitation became complete just after the stoichiometrical amount of sodium phosphate, 40 c.c., had been added. The change in  $p_H$  with the excess of reactant shows that a basic phosphate had been precipitated, and the exceptional change after 4 equivs. of sodium phosphate had been added indicates that the precipitate underwent rapid hydrolysis. The  $p_H$ , 8.07, attained when this change began was that which would have been produced by a solution of phosphoric acid neutralised by caustic soda almost to  $\text{Na}_2\text{HPO}_4$ , *i.e.*, in the present reaction, according to the equation  $2\text{Na}_3\text{PO}_4 + \text{H}_3\text{PO}_4 = 3\text{Na}_2\text{HPO}_4$ . Hence the equivalent which was in excess of the amount necessary to form the normal chromium phosphate required approximately one-sixth of a molecule of phosphoric acid to bring the  $p_H$  of the solution up to about 8, and therefore the amount of phosphoric acid in combination with the precipitate at that stage was about five-sixths of that present in the normal phosphate. It has been suggested (*J.*, 1925, 127, 2120) that in the ordinary violet chromium salts approximately one equiv. of acid radical exists in a looser kind of combination than do the other two equivs., so that chromium sulphate in solution might be represented as  $\text{Cr}_2(\text{SO}_4)_2(\text{OH})_2 \text{---} \text{H}_2\text{SO}_4$ , and therefore on treatment with trisodium phosphate the first reaction to take place would be the replacement of this loosely bound molecule of sulphuric acid by two-thirds of a molecule of phosphoric acid, and unless the solubility-product requirements of the normal chromium phosphate are simultaneously satisfied no precipitation would ensue, although a change in hydrogen-ion concentration would be produced, comparable with that set up in the reactions of chromium salts which involve the precipitation of basic salts.

The  $p_H$ , 5.66, at which the zinc phosphate precipitate began to form was a little higher than that required by zinc hydroxide, *i.e.*, 5.20, but reference to the hydroxide precipitation curve (*Britton, J.*, 1925, 127, 2125) shows that the  $p_H$  during the main part of the precipitation was 6, whereas the phosphate curve shows a slightly lower  $p_H$ , *viz.*, 5.7.

The *E.M.F.*'s recorded in the reaction with calcium chloride up to

the addition of 7 c.c. of sodium phosphate tended to be low initially but slowly increased to steady values; for larger volumes of sodium phosphate the voltages given primarily appeared to be reproducible. The stoichiometrical amount of sodium phosphate was 71.6 c.c., and this, as seen from the curve, gave rise to a hydrogen-ion concentration which was represented by a point of the inflexion corresponding to the completion of precipitation as the normal calcium phosphate. The greater part of the precipitation occurred between  $p_H$  9.5 and 10 and, as will be seen from the sodium hydroxide titration curve (Fig. 1), such a  $p_H$  corresponds to equilibria involving a predominance of  $\text{HPO}_4''$  and very few  $\text{PO}_4'''$  ions, thus  $\text{HPO}_4'' + \text{OH}' \rightleftharpoons \text{PO}_4''' + \text{H}_2\text{O}$ , which must have been given by the hydrolysis of the tricalcium phosphate into the dicalcium salt:  $\text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{O} = 2\text{CaHPO}_4 + \text{Ca}(\text{OH})_2$ . The difference between the  $p_H$ 's which prevailed during the precipitation of calcium phosphate in series I and II was due to suppression of the hydrolysis in the former case by the presence of a small amount of partly neutralised phosphoric acid, whereas this was absent in the double decomposition. There is, however, very little difference in the  $p_H$ 's of precipitation of the phosphates of the weaker base-forming metals, *e.g.*, zinc and cobalt.

The precipitation from the magnesium sulphate solution is of interest for two reasons. First, the inflexion indicating the end of precipitation did not appear when the stoichiometrical amount of sodium phosphate had been added, *viz.*, 40 c.c., but occurred with about  $1\frac{1}{2}$  times that quantity. Secondly, the solution from which the precipitate had separated was even more alkaline than that in the calcium reaction, the  $p_H$  at which the precipitate began to form being 9.76. The exact incidence of the inflected part depended on the efficiency of agitation of the reaction mixture and on the time allowed before measuring the *E.M.F.* The broken line was obtained by allowing longer time, and the inflexion began at 60 c.c., whereas the first curve was undergoing inflexion with that amount. A  $p_H$  of 9.76 must have been produced by the same kind of ionic equilibria as in the calcium phosphate precipitation, in which, however, there was a greater proportion of phosphate ions. The amount of sodium phosphate required to effect precipitation suggests the reaction  $\text{MgSO}_4 + \text{Na}_3\text{PO}_4 = \text{MgHPO}_4 + \text{NaOH} + \text{Na}_2\text{SO}_4$ , but the fact that the  $p_H$  remained almost stationary at 10 throughout the course of precipitation shows that the concentration of free alkali was relatively small. Analyses of the mother-liquors showed that the sodium hydroxide had combined with the precipitated magnesium phosphate in the form of a double phosphate,  $\text{MgNaPO}_4$ , and it was therefore the hydrolysis of this double phosphate into magnesium

hydrogen phosphate and sodium hydroxide which determined the  $p_H$  throughout the precipitation.

*Note on the Phosphate Separation.*

The observations made in the course of these electrometric titrations afford a satisfactory explanation of the procedure adopted in qualitative analysis for the removal of phosphates. The phosphate precipitation  $p_H$ 's are functions of the concentrations of both the metallic and the phosphate ions, and the use of dilute solutions tends to keep the concentrations of both the bases and phosphoric acid comparatively small, and thereby fixes within narrow limits the  $p_H$  at which the various phosphates are precipitated as the free acid is gradually neutralised and the solution made alkaline. The hydrogen-ion concentrations which prevailed during the formation of the phosphate precipitates (Fig. 2) are approximately those which would be set up if the phosphoric acid had been present in the solution and was subsequently neutralised with alkali. In the "basic acetate" method of removing phosphates, the solution, before treatment with ferric chloride solution, is buffered at about  $p_H$  5 by the acetic acid and an excess of either sodium or ammonium acetate. Fig. 2 shows that the only phosphates to be precipitated from solutions more acid than  $p_H$  5 are those of zirconium, thorium, aluminium, beryllium, and chromium. Ferric phosphate is also precipitated from very acid solutions. The phosphates and hydroxides which are precipitated from solutions of  $p_H$  higher than 5 are those of zinc, manganese, calcium, and magnesium, to which should be added cobalt, nickel, strontium, barium, and many of the rare earths. It appears, therefore, that as the  $p_H$  of the phosphate solution is raised to 5, the phosphates precipitated will be, first, ferric, then aluminium, and finally chromium, but if the quantity of phosphoric acid in the solution is inadequate to form any or all of these phosphates, then the acid will combine with the bases in the order in which they are precipitated, and consequently the hydroxides themselves may be precipitated. Hence, by having a quantity of these three bases, and preferably of ferric hydroxide, more than sufficient to combine with the total amount of phosphoric acid present, the phosphate will be completely removed without precipitation of the bases belonging to the subsequent groups. Acetic acid has a marked tendency, owing to the formation of soluble basic acetates, to retain the hydroxides in solution even though the  $p_H$ 's at which they are normally precipitated may have been exceeded (*vide* Britton, J., 1926, 269). These acetate solutions are, however, completely decomposed on boiling, although long boiling may be necessary if too much acetate be used.



*Summary.*

(1) The dissociation constants,  $K_1 = 0.94 \times 10^{-2}$ ,  $K_2 = 1.4 \times 10^{-7}$ , and  $K_3 = 2.7 \times 10^{-12}$ , at  $20^\circ$ , have been shown to satisfy the hydrogen-electrode titration curve of phosphoric acid by sodium hydroxide.

(2) The hydrogen-electrode curves of phosphoric acid in course of neutralisation by the alkaline earths show that this process at first goes beyond the limits fixed by the very small solubilities of the alkaline-earth phosphates, which later become precipitated, although a considerable time must elapse before equilibrium between the precipitates and the solutions is established.

(3) The presence of sucrose in a phosphoric acid solution prevents the exceptional increase in hydrogen-ion concentration which ordinarily occurs during precipitation with calcium hydroxide.

(4) Calculations from Bassett's data for the system  $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$  at  $25^\circ$  show that calcium phosphate is not precipitated from solutions which are more acid than  $p_H$  5.5. Probable values for the solubility products of di- and tri-calcium phosphates have been found.

(5) Hydrogen-electrode titrations with trisodium phosphate of salt solutions of zirconium, thorium, aluminium, beryllium, chromium, zinc, manganese, magnesium, and calcium have been described, in which it has been shown that all, except the last two, yield basic phosphates. Magnesium forms a double phosphate with sodium. The redissolution of the aluminium precipitate in an excess of precipitant has been traced to the formation of sodium aluminate.

(6) The importance of the  $p_H$  data relating to the precipitation of phosphates has been emphasised in respect of (a) the application of phosphatic fertilisers to soils, and (b) the removal of phosphates in qualitative analysis.

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