Complexes involving Tervalent Iron and Orthophosphoric Acid. Part III.*
The System Ferric Oxide–Phosphoric Oxide–Water at 25°.

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Phase-diagram studies in the range from 0·35% to 66% of phosphoric oxide have shown the following to be the stable solid phases at 25° :

$Fe_2O_3,P_2O_5,5H_2O$; $Fe_2O_3,2P_2O_5,8H_2O$; $Fe_2O_3,3P_2O_5,10H_2O$; $Fe_2O_3,3P_2O_5,6H_2O$. All are lilac or pink crystalline solids. The last is probably $H_3[Fe(HPO_4)_3]$, but the constitution of the others is less certain. Two metastable states have been observed in the more dilute solutions, and diferric tetraphosphate, $Fe_2P_4O_{13}$, has been found as a metastable solid phase in the more concentrated solutions.

Anion-exchange studies have shown the presence in the solutions of the triphosphatoferric complex which, together with free phosphate, is adsorbed by the exchanger. The complex is adsorbed as the $[Fe(HPO_4)_3]^{3-}$ ion, but when the resin is washed it is converted into the $[Fe(PO_4)_3]^{6-}$ ion. No definite evidence was obtained of adsorption of a diphosphatoferric complex, and cation-exchange experiments failed to show the presence of the $[FeHPO_4]^+$ ion.

COMPLETE phase-diagram studies of the system at 40° (Bailer, Thesis, Leipzig, 1930) and at 70° (Carter and Hartshorne, *J.*, 1923, **123**, 2223) have been reported, but only incomplete data are available for 25° (Cameron and Bell, *J. Phys. Chem.*, 1907, **11**, 363; Carter and Hartshorne, *loc. cit.*). At 25°, however, not only have persistent metastable states been encountered (Carter and Hartshorne, *loc. cit.*; Part I, *J.*, 1952, 2316), but an extensive system of parallel tie-lines has been reported for the solid phases in equilibrium with the solutions containing up to 10% of phosphoric oxide. Further, some at least of the solid phases have been attributed complex structures (Weinland and Ensgraber, *Z. anorg. Chem.*, 1914, **84**, 340; Carter and Hartshorne, *loc. cit.*). It seemed important therefore to include in the present series of studies a thorough examination of the system.

RESULTS

Phase-diagram Studies.—A study of the system at 25° for the range of solutions up to 66% of phosphoric oxide (Table 1*a*, Fig. 1) has indicated the following as stable solid phases : (A) $Fe_2O_3,P_2O_5,5H_2O$, the tertiary phosphate, deep lilac, minute, hexagonal plates. (B) $Fe_2O_3,2P_2O_5,8H_2O$, pale pink, needle-shaped crystals. (C) $Fe_2O_3,3P_2O_5,10H_2O$, small, deep pink crystals in regular-shaped hexagons. (D) $Fe_2O_3,3P_2O_5,6H_2O$, small, pale pink crystals in distorted hexagons.

The descriptions of the compounds agree with those given by Carter and Hartshorne except that these workers could discern no crystalline form in the tertiary phosphate. Weinland and Ensgraber (*loc. cit.*), however, describe it as crystalline. Although Carter and Hartshorne later (*J.*, 1926, 363) revised the formula of this compound to $Fe_2O_3,P_2O_5,4H_2O$, our data indicate a penta- rather than a tetra-hydrate. The negative temperature coefficient of solubility reported for this tertiary phosphate by Carter and Hartshorne (*J.*, 1923, **123**, 2223) has been confirmed. The number and nature of the solid phases and their ranges of stability are in good agreement with the published data for 40° and 70°, when the effect of temperature is taken into account, except that the compound, $Fe_2O_3,2P_2O_5,10H_2O$, found at 40° by Bailer (*loc. cit.*) does not appear in the system at 25° or at 70°.

In studying the region of the diagram from 0·3% to 26% of phosphoric oxide, 5M-phosphoric acid was saturated with the tertiary phosphate at temperatures not exceeding 80°, cooled, and diluted with the required amount of water, and the resulting clear solution allowed to reach equilibrium at 25°. The following stages were noticed in the attainment of equilibrium : (1) Separation of a compound, $Fe_2O_3,3P_2O_5,xH_2O$ (where x

Fig. 1. Fe_2O_3–P_2O_5–H_2O at 25°. *Stable equilibria.*
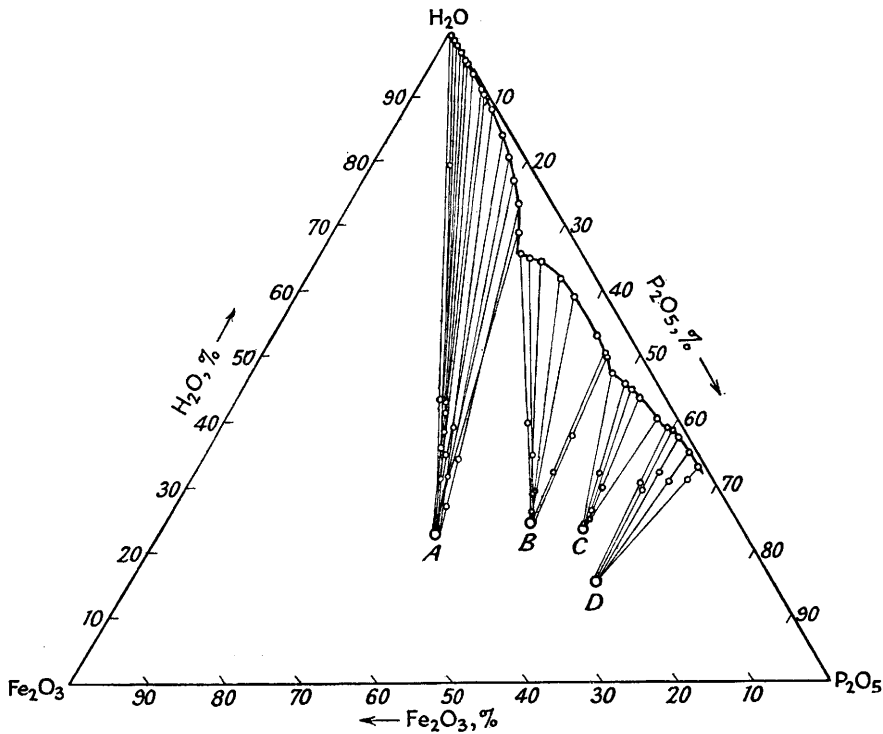
Table 1. *The system ferric oxide–phosphoric oxide–water at 25°.*

Solutions			Moist solids *		
P_2O_5, %	Fe_2O_3, %	d	P_2O_5, %	Fe_2O_3, %	Type
(a) Stable equilibrium					
0·350	0·003	1·00	26·95	30·01	
1·312	0·015	1·00	10·20	10·21	
2·32	0·033	1·00	26·76	29·03	
3·34	0·053	1·03	33·00	37·02	
4·39	0·075	1·01	27·88	29·70	
4·61	0·081	1·04	29·81	32·08	
6·40	0·139	1·05	28·51	30·28	
7·90	0·212	1·05	30·67	33·57	A
9·23	0·268	1·07	30·03	31·65	
11·50	0·479	1·07	30·60	31·98	
15·02	1·009	1·07	31·68	30·00	
17·23	1·92	1·07	31·91	33·50	
19·96	3·12	1·10	36·14	37·12	
22·13	4·20	1·15	34·02	31·86	
24·50	6·35	1·19	34·01	34·53	
26·61	7·92	1·32	40·5	19·99	
28·1	7·00	—	46·2	24·8	
29·9	5·72	—	43·6	21·9	
33·9	4·50	1·42	46·9	24·4	B
37·0	4·11	—	47·6	26·3	
43·0	4·09	—	—	—	
45·2	4·46	1·61	47·6	20·3	
45·8	4·51	—	47·4	15·02	
48·1	4·78	1·70	55·4	20·4	
50·3	4·05	1·76	53·7	14·3	
51·5	3·61	—	55·6	18·1	C
53·8	3·14	—	55·1	15·0	
57·3	2·62	—	55·8	19·5	

Solutions			Moist solids *		
P_2O_5, %	Fe_2O_3, %	d	P_2O_5, %	Fe_2O_3, %	Type
59·1	1·98	—	59·8	9·51	
60·0	1·44	1·86	60·4	9·89	
61·5	1·114	—	61·5	6·21	D
64·0	0·919	—	63·5	5·78	
66·3	0·907	—	65·6	3·23	
(b) Metastable equilibrium I : 0—23% P_2O_5					
3·71	1·31	—	16·94	6·02	
10·08	3·11	—	23·11	8·24	D†
21·43	7·32	1·25	40·50	15·29	
23·09	7·67	1·26	42·09	14·45	
(c) Metastable equilibrium II : 0—20% P_2O_5					
2·43	0·034	1·02	23·6	24·2	
5·60	0·202	1·07	35·3	32·9	
9·15	1·50	—	31·8	27·0	
14·88	3·21	—	34·2	23·8	
18·45	6·16	1·19	36·1	24·0	
19·06	5·93	1·20	35·0	21·7	
(d) Metastable equilibrium III : 50—64% P_2O_5					
50·1	16·32	1·62	56·1	25·3	
55·7	10·92	—	61·1	28·1	E
59·8	7·19	—	62·1	24·0	
63·6	4·22	2·37	63·9	26·4	

* Solid phase : A = $Fe_2O_3,P_2O_5,5H_2O$.   B = $Fe_2O_3,2P_2O_5,8H_2O$.   C = $Fe_2O_3,3P_2O_5,10H_2O$.   D = $Fe_2O_3,3P_2O_5,6H_2O$.   E = $Fe_2P_4O_{13}$.

† The exact degree of hydration cannot be determined from the tie-lines.

is **6**, probably), usually after **4—5** weeks (Table 1*b*, Fig. 2*a*).   (2) Conversion of this into a solid phase represented by one of the series of parallel tie-lines—after **6—10** weeks in the thermostat bath (Table 1*c*, Fig. 2*b*).   (3) Conversion of this last into the stable tertiary phosphate—usually requiring **10—15** weeks from the start, together with frequent stirring

FIG. 2.

(*a*) *Metastable* $Fe_2O_3,3P_2O_5,6H_2O$, D

(*b*) *'Parallel lines'*

(*c*) *Stages in attaining equilibrium*

(*d*) *Ferric tetraphosphate* $[Fe_2P_4O_{13}]$, E

$Fe_2O_3,P_2O_5,5H_2O$ Previous work ●—— Present work ○——

'*Parallel lines*'.........--▲------△---

$Fe_2O_3,3P_2O_5,6H_2O$ Previous work --■-- Present work --□--

$Fe_2P_4O_{13}$.........................——▽——
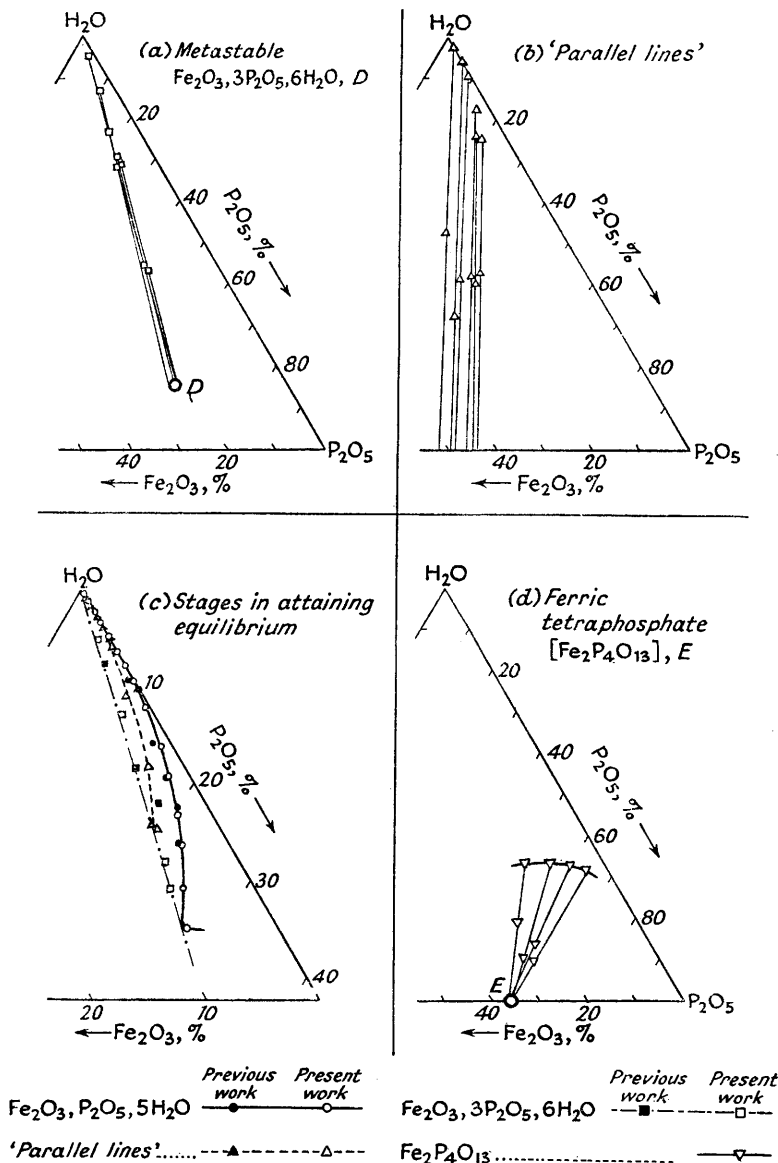
of the mixture (Table 1*a*, Fig. 1).   The times taken to reach the various stages depended on both the concentration and the extent of stirring.   With the exception of one result, the different stages can be attributed definite solubilities (Fig. 2*c*).

In the region of solutions containing 50—66% of phosphoric oxide, it was found that the acid would, at temperatures of 100° or higher, dissolve a considerable amount of the tertiary phosphate, but that, if this was allowed to happen, the resulting solution was brown instead of the usual pink or lilac colour.   Crystallisation occurred only slowly from

such solutions at 25° and instead of yielding orthophosphates gave yellowish-white, octagonal crystals of the anhydrous tetraphosphate, $Fe_2P_4O_{13}$, as a metastable phase (Table 1*d*, Fig. 2*d*). This compound was extremely hygroscopic and on exposure to air soon gave pale pink, needle-shaped crystals similar to those of $Fe_2O_3,2P_2O_5,8H_2O$.

Anion-exchange Experiments.—The adsorption of iron and phosphate by Amberlite I.R.A. 400-phosphate from stable solutions has been determined under equilibrium con-

FIG. 3. *Adsorption of iron and phosphate by* I.R.A. 400-PO_4.
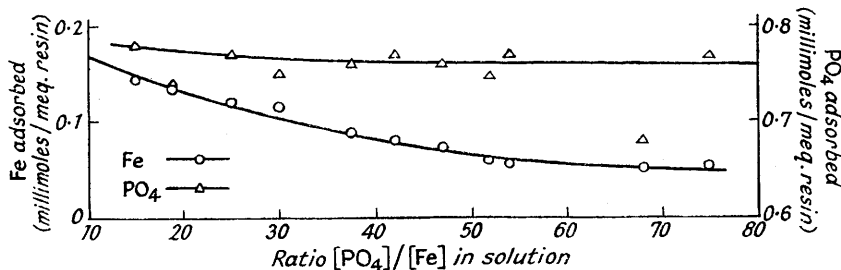
ditions. Except with one solution, shown by the present work to have been in metastable equilibrium, the previous results (Part I, *loc. cit.*) have been confirmed and also extended to the region of more dilute solutions (Table 2*a*). The relative amounts of H_2PO_4' and HPO_4'' ions retained by the resin from phosphoric acid solutions of corresponding concentrations have also been determined (Table 2*b*). By assuming that the free phosphate is adsorbed in a similar manner from the ferric phosphate solutions, attempts have been made to account for the capacity of the resin in terms of the adsorption of various complexes

TABLE 2*a*. *Adsorption of iron and phosphate by* I.R.A. 400-*phosphate* (1·00 g.) *from ferric phosphate solutions* (100 ml.).

Solution			Resin					
P_2O_5, %	$\dfrac{[P_2O_5]}{[Fe_2O_3]}$	Capacity, milli-equiv./g.	Mols. adsorbed/equiv. resin : Fe	PO_4	Capacity accounted for, % * A	B	C
1 †	110	2·21	0·009	0·632	98	95	97
2·3	86·2	1·95	0·022	0·622	98	92	95
4·4	66·2	1·97	0·041	0·607	99	86	93
5·0	58·2	1·82	0·053	0·590	98	82	90
10·0	33·5	2·07	0·109	0·566	101	69	86
15·0	17·5	1·98	0·169	0·570	111	61	87
20·0	8·2	1·89	0·184	0·563	112	57	86

* Assuming the following to be adsorbed : A = $[Fe(PO_4)_3]^{6-}$; B = $[Fe(HPO_4)_3]^{3-}$; C = $[Fe(PO_4)_2]^{3-}$; together with, in each case, H_2PO_4' and HPO_4'' in the proportions indicated by the results in Table 2*b*.   † 500 ml. of solution, 0·25 g. of resin.

TABLE 2*b*. *Adsorption of phosphate by* I.R.A. 400-*phosphate* (1·00 g.) *from phosphoric acid solutions* (100 ml.).

Solution : P_2O_5, %	Capacity, milli-equiv./g.	Resin : Mols. adsorbed/equiv. resin : PO_4	Phosphate adsorbed as HPO_4'', % *
5	1·93	0·654	51·7
10	1·84	0·660	51·5
15	2·07	0·643	55·5
20	1·99	0·643	55·5

* Remainder as H_2PO_4'.

together with that of free phosphate (Table 2*a*). With the possible exception of the solution containing 1% phosphoric oxide, it is evident that $[Fe(PO_4)_3]^{6-}$ must be the principal complex species retained. With the solutions containing more than 10% of phosphoric oxide a second species must also be adsorbed, but from the conditons under which this occurs it is presumably the $[Fe(HPO_4)_3]^{3-}$ ion rather than the $[Fe(PO_4)_2]^{3-}$ ion that is involved.

In another series of experiments the adsorption by I.R.A. 400-phosphate of iron and phosphate from a solution 0·1M in iron and 1·5M in phosphate (10% P_2O_5), as well as from mixtures of this solution with 1·5M-phosphoric acid, was studied. Although this series represented a transition from supersaturated to unsaturated solutions, at a molar ratio of phosphoric oxide to ferric oxide of 30 : 1, no break in the adsorption of either iron or phosphate occurred at this point (Fig. 3).

Cation-exchange Experiments.—Batch, as distinct from column, experiments have now been carried out with stable solutions in the range 1—15% of phosphoric oxide. No adsorption of phosphate was observed and the adsorption of iron by the exchanger (Zeo-Karb 225-H) was found to be small and to fall with decreasing pH of the solutions (Table 3). Thus the concentration of the ion $[FeHPO_4]^+$ must be appreciably less than in the solutions containing chloride and phosphate (Part II).

TABLE 3. *Adsorption of iron (and phosphate) by Zeo-Karb 225-H (0·500 g.) from ferric phosphate solutions (100 ml.).*

Solutions :			Resin		
P_2O_5, %	$\dfrac{[P_2O_5]}{[Fe_2O_3]}$	pH	Capacity, milli-equiv./g.		Mols. Fe adsorbed/equiv. resin : *
1 †	110	1·48	3·71		0·196
5	58·2	0·90	3·71		0·076
10	33·5	0·45	3·72		0·032
15	17·5	0·24	3·71		0·031

* No phosphate adsorbed.   † 500 ml. of solution.

DISCUSSION

Nature of the Solutions.—It is evident from the anion-exchange studies (Table 2) that the triphosphatoferric complex is retained by the resin and must, therefore, be present in the solutions. This conclusion, which is in agreement with those reached in Part I, receives further support from the observation that, on dilution of a more concentrated ferric phosphate solution, the compound that separates first is one containing phosphate and iron in the molar ratio 3 : 1.

Although it might be expected to be adsorbed in competition with the H_2PO_4' ions, little, if any, of the diphosphatoferric complex, $[Fe(PO_4)_2]^{3-}$, was found to be retained. Indeed, the following facts all suggest that the concentrations of complexes with fewer phosphato-groups than three may be very low : (1) the very low concentration of $[FeHPO_4]^+$ as shown by the cation-exchange experiments (Table 3); (2) the more dilute solutions, where complexes with fewer phosphato-groups might be expected to predominate, are only stable when the ratio of phosphoric oxide to ferric oxide in them is very high (Table 1a); (3) solutions in which the $[FeHPO_4]^+$ ion has been shown to exist and in which the presence of the $[Fe(H_2PO_4)_2]^-$ ion has been postulated are all colourless, whereas the pure ferric phosphate solutions of corresponding concentrations are pink or lilac.

The absence of any break in the adsorption of iron or phosphate in passing from supersaturated solutions to unsaturated ones (Fig. 3) indicates that the species present in both types of solution are the same—even in the metastable solutions the ratio PO_4 : Fe is always 3 : 1 or greater. The results recorded in Fig. 3 (which were obtained by washing the resin with a fixed amount of water, instead of to neutrality to methyl-orange as with the other experiments) are only explicable in terms of the capacity of the resin by assuming that some 60—80% of the triphosphatoferric ion is adsorbed in the tribasic form, $[Fe(HPO_4)_3]^{3-}$, even when allowance is made for the fact that under these conditions 65% of the free phosphates is adsorbed as H_2PO_4' ions. It seems likely that the ions adsorbed from solution are $[Fe(HPO_4)_3]^{3-}$ and H_2PO_4' and that these are converted into $[Fe(PO_4)_3]^{6-}$ and a mixture of H_2PO_4' and HPO_4'' respectively on washing the resin. The reactions involved are presumably of the types :

$$2RH_2PO_4 + nH_2O = R_2HPO_4 + H_3PO_4, aq.$$
$$R_3[Fe(HPO_4)_3] + 3RH_2PO_4 + nH_2O = R_6[Fe(PO_4)_3] + 3H_3PO_4, aq.$$
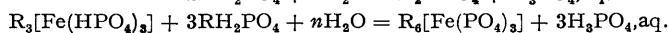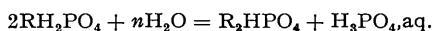
where R represents 1 equiv. of the anion-exchanger.

The facts that the triphosphatoferric complex is not decomposed on prolonged washing of the resin and that it is the compound first produced even on high dilution of the more concentrated ferric phosphate solutions show that it is not readily hydrolysed.

Nature of the Solid Phases.—The pink or lilac colour of the stable solutions is also characteristic of the solid phases in equilibrium with them, and this may indicate, although it does not prove, a similarity of constitution. Weinland and Ensgraber (*loc. cit.*) have already suggested that the solid phases are in fact complex.

It seems likely that the compound, $Fe_2O_3,3P_2O_5,6H_2O$, is a complex such as $H_3[Fe(HPO_4)_3]$ or $H_6[Fe(PO_4)_3]$, since it often separates first from solutions containing such a complex even when it is not the stable solid phase. The corresponding decahydrate presumably has a similar structure.

Although Weinland and Ensgraber (*loc. cit.*) assigned the structure $H_3[Fe(PO_4)_2]$ to the compound $Fe_2O_3,2P_2O_5,8H_2O$, we have found no evidence of the corresponding anion in the solutions. Likewise, the tertiary phosphate which these authors regard as being $Fe[Fe(PO_4)_2],5H_2O$ could equally well be $Fe_2[Fe(PO_4)_3],7\frac{1}{2}H_2O$. It is evident that little further can be learnt of the structures of these compounds until a complete X-ray examination has been made, and it is unfortunate that in his study of the tertiary compound Caglioti (*Atti R. Accad. Lincei*, 1935, **22**, 146) heated it first to 600° for 2 hr.

Cole and Jackson's evidence (*J. Phys. Coll. Chem.*, 1950, **54**, 128) for regarding the tertiary phosphate as a dihydroxy-dihydrogen phosphate, $Fe(OH)_2H_2PO_4$, is not, in our opinion, conclusive. In any case this structure seems hardly likely for a compound which crystallises from solutions having a pH value as low as 0·24 (cf. Table 3).

Carter and Hartshorne accounted for the parallel tie-lines by assuming that the tertiary phosphate adsorbed more or less acid, according to the concentration in the liquid phase. Since such adsorption would presumably depend on the surface area of the solid, it would not lead to parallel tie-lines. Further, it is difficult to reconcile their theory with the fact that the parallel tie-line system gives way to the tertiary phosphate, without any adsorbed acid.

The parallel tie-lines could arise from the formation of solid solutions between the tertiary phosphate and one of the more acid compounds. Another possibility is that the compound, $H_6[Fe(PO_4)_6]$, which separates first, acts as a cation-exchanger and exchanges its hydrogen ions for ferric ions in the solution, to an extent determined by the acid concentration.

The change in colour, and the separation of the anhydrous tetraphosphate $Fe_2P_4O_{13}$ (Table 1*d*) in place of an orthophosphate, both show that strong heating produces a change in the nature of the species present in solution. We therefore took particular care in the equilibrium studies not to heat the solutions above 80°. The existence of a compound $Fe_2O_3,2P_2O_5$ was first mentioned by Millot (*Compt. rend.*, 1876, **82**, 89), but was later questioned by Brasseur (*ibid.*, 1936, **202**, 761; cf., however, *idem, ibid.*, 1940, **211**, 258). Recently, Thilo and Rätz (*Z. anorg. Chem.*, 1949, **260**, 255) have shown that tetraphosphates may exist under certain conditions, and they obtained evidence for a ferric salt, as well as for other heavy-metal compounds.

It is surprising that the compound $Fe_2O_3,2P_2O_5,10H_2O$, found in the system at 40° by Bailer, should not occur at either 25° or 70°. We suspect that Bailer's results may be in error here, since he used a commercial ferric phosphate as starting material—in spite of the fact that Carter and Hartshorne had previously pointed out that such material always contains alkali-metal impurities. The yellowish-white colour of the compound, which distinguishes it from the other stable phases, suggests that it may contain alkali. We have, in fact, observed that the addition of a very small amount of alkali-metal dihydrogen phosphate to a stable ferric phosphate solution (containing 26% of P_2O_5) caused the separation of a considerable amount of yellowish-white solid. The use of an impure starting material would have a significant effect on the results only where a considerable amount of it was dissolved, which would be the case in the region where the compound $Fe_2O_3,2P_2O_5,10H_2O$ was reported to occur.

C

<div align="center">EXPERIMENTAL</div>

The experimental procedure was the same as in Parts I and II with the following exceptions.

Preparation of Solutions for Phase-diagram Studies.—Solutions containing more than 25% of phosphoric oxide were made by saturating phosphoric acid solutions of different concentrations with the tertiary phosphate at temperatures not exceeding 80°. These solutions were cooled rapidly and allowed to reach equilibrium at 25°. Alternate tubes were stirred daily for 4 weeks and then allowed to settle for one week, and the others were stirred for 6 weeks and allowed to settle for one. A smooth solubility curve was taken as a criterion of equilibrium.

For the more dilute solutions, 5M-phosphoric acid was saturated with the tertiary phosphate at temperatures below 80°, and the resulting clear solution cooled. Portions of this were diluted to 30—150 ml. (as determined by the need to obtain sufficient solid for analysis) and allowed to crystallise at 25°. In the equilibrium experiments (Table 1a) the mixture was frequently stirred, and the crystalline mass broken up. Equilibrium was assumed to be reached on two counts : (1) the tertiary phosphate was the solid phase over the whole range and showed throughout a definite crystalline form; (2) no evidence of any further change was noted in any solutions left for between twelve and fifteen weeks.

Apparatus.—For the solutions containing more than 50% of phosphoric oxide, glass-stoppered vessels were used in place of those with rubber bungs.

Analysis.—The moist solids were separated from the liquid phases by filtration through a sintered-glass filter. Whenever possible, an approximate value for the density of the liquid was obtained by using a definite volume of liquid for analysis. All solids were examined microscopically and analysed by the methods previously described (*loc. cit.*).

Anion-exchange Experiments.—Apart from the experiments recorded in Fig. 3, where 800 ml. of water were used, the resin was always washed until the washings were neutral to methyl-orange before determination of the species adsorbed. Thorough washing always preceded capacity determinations.