433. *Complexes involving Tervalent Iron and Orthophosphoric Acid. Experiments with Ion-exchange Resins.*

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It is shown that iron can be removed from ferric phosphate solutions by using either cation-exchange or anion-exchange resins. Batch experiments with the phosphate form of the anion-exchange resin indicate the presence in the solutions of a complex containing three phosphate groups per iron atom. Support for this conclusion is provided by the examination of both stable and metastable states of the system, ferric oxide–phosphoric oxide–water.

The phosphate group presumably acts as a bidentate group, but it is not certain whether the complex is $H_3[Fe(HPO_4)_3]$ or $H_6[Fe(PO_4)_3]$. The evidence for the existence of complexes containing fewer phosphate groups is much less definite.

ALTHOUGH the literature provides abundant evidence of the formation of complexes between the ferric ion and orthophosphoric acid, there seems to be little agreement as to their nature, or even their number. The most obvious indication is provided by the decolorising action of phosphoric acid on solutions of ferric chloride. Carter and Clews (*J.*, 1924, **125**, 1880) showed that phosphoric acid lowers the oxidation potential of the ferrous–ferric system, and Bonner and Romeyn (*Ind. Eng. Chem.*, *Analyt.*, 1931, **3**, 85) observed that the reversible reaction $Fe^{++} + \frac{1}{2}I_2(aq.) \rightleftharpoons Fe^{+++} + I^-$ went to completion in the presence of phosphoric acid.

The interference by phosphates in the colorimetric determination of ferric iron with thiocyanates (Dupré, *Chem. News*, 1875, **32**, 5) suggests that the ferric phosphate complex is at least comparable in stability with the ferric thiocyanate complex. That the concentration of ferric ions is still large enough to be detected, however, is shown by the formation of Prussian-blue on addition of potassium ferrocyanide to ferric phosphate solutions.

The widely differing views as to the number and nature of the complexes formed put forward by various workers may be summarised as follows: (1) The complexes are ferriphosphoric acids, such as $H_3[Fe(PO_4)_2]$ and $H_6[Fe(PO_4)_3]$ (Weinland and Ensgraber, *Z. anorg. Chem.*, 1914, **84**, 340). (2) Complexes, such as $H_3[Fe(PO_4)Cl_3]$, are present in solutions containing chloride ions (Dede, *ibid.*, 1922, **125**, 28; Ricca and Meduri, *Gazzetta*, 1934, **64**, 235). (3) The complex is $[FeHPO_4]^+$ (Landford and Kiehl, *J. Amer. Chem. Soc.*, 1942, **64**, 291). (4) The complex is $[FeH_2PO_4]^{++}$, even in solutions containing chloride ions (Jensen, *Z. anorg. Chem.*, 1934, **221**, 1). (5) No complex is formed, but, rather, a weak electrolyte ranging in composition from $FePO_4$ to $Fe(H_2PO_4)_3$ (Bonner and Romeyn, *loc. cit.*).

Weinland and Ensgraber (*loc. cit.*) reported various salts of ferri-di- and -tri-phosphoric acids, such as $NaH_2[Fe(PO_4)_2],H_2O$ and $NaH_5[Fe(PO_4)_3],H_2O$. Two acid ferric phosphates previously reported by Erlenmeyer (*Annalen*, 1878, **194**, 176) were considered to be the parent "acids" of these salts. Dede (*loc. cit.*) and, later, Ricca and Meduri (*loc. cit.*) found that solutions containing ferric chloride and phosphoric acid showed much higher conductivites than those calculated on the basis of a simple additive law. These results were interpreted as indicating formation of a strong acid, $H_3[Fe(PO_4)Cl_3]$, which in the presence of excess of phosphoric acid was converted into a pure phosphate complex. No salts of the chloroferriphosphoric acid were isolated by Dede, but Ricca and Meduri reported the formation of a silver salt, $Ag_3[Fe(PO_4)Cl_3]$.

Jensen (*loc. cit.*), from solubility data, decided, on the contrary, that, even in solutions containing chloride ions, only pure phosphato-complexes were formed. The results of Dede and of Ricca and Meduri were explained by postulating the formation of the ion $[FeH_2PO_4]^{++}$.

Lanford and Kiehl (*loc. cit.*) used the decrease in the colour of the ferric thiocyanate complex (assumed to be $FeCNS^{++}$), effected by addition of phosphoric acid to solutions containing ferric nitrate and sodium thiocyanate, to deduce the ratio of iron to phosphorus in the complex. Their results indicated the formation of the complex $[FeHPO_4]^+$. This work has been criticised by Banerjee (*J. Indian Chem. Soc.*, 1950, **27**, 417) on the grounds that thiocyanates are unsuitable for the purpose because of the presence of several ferric thiocyanate complexes the individual concentrations of which will vary with the concentrations of the reactants. In a series of thermometric, conductometric, and colorimetric titrations of ferric chloride with phosphoric acid, this author found breaks in the titration curves which he attributed to the formation of $[FeHPO_4]^+$ and $[Fe(HPO_4)_2]^-$. The results of two ionic-transport experiments were submitted as further evidence in support of these formulæ.

Although a possible explanation for such a diversity of opinion could be that all the complexes reported do exist, but under different conditions, yet this does not seem likely since four of the complexes, $[Fe(HPO_4)_2]^-$, $[Fe(H_2PO_4)]^{++}$, $[FeHPO_4]^+$, and $[Fe(PO_4)Cl_3]^{3-}$, have all been reported as being present in solutions containing chloride. In fact, all but the first are supposed to be present in solutions containing equimolecular amounts of ferric chloride and phosphoric acid. Consequently, another explanation must be sought.

Another possibility that has not apparently hitherto been taken into account is that several complexes may co-exist in solution in proportions depending on the concentrations of the reactants. It would seem likely that the ferric phosphate complexes are derived from the $[Fe(H_2O)_6]^{+++}$ complex by the substitution of phosphate ions, and possibly of other anions present in solutions also, for the water molecules in the complex. Weinland ("Einführung in die Chemie der Komplex-Verbindungen," Stuttgart, 1924, pp. 145, 221) and Jensen (*loc. cit.*) have expressed the view that the phosphate group is likely to occupy two co-ordination positions. Hence, with complexes containing one or two phosphate groups, it could be assumed, in the absence of other ions, that the remaining co-ordination positions were occupied by water molecules. Most of the evidence available, however, is based on studies where either chloride or thiocyanate ions were also present. In such cases, complications due to the co-ordination of these ions in the complex are likely to arise, and the lack of agreement reported may be due, in part at least, to this. Consequently, a study of the ferric phosphate system in the absence of interfering ions seems desirable.

Carter and Hartshorne (*J.*, 1923, **123**, 2223) examined the system ferric oxide–phosphoric acid–water, but primarily in the light of the phase rule, and no evidence was offered of complex formation in the liquid phase. A reinvestigation of the system with this end in view was therefore undertaken.

Present Work.—The use of ion-exchange resins for the study of ferric phosphate complexes was suggested by their wide application in separating both simple and complex ions from solution (see, *e.g.*, "Ion Exchange, Theory and Application," ed. Nachod, Academic Press Inc.; Duncan and Lister, *Quart. Reviews*, 1948, **2**, 307). As far as possible, saturated solutions in the system ferric oxide–phosphoric oxide–water have been used in these experiments in order to avoid any undue excess of phosphoric acid in solution. Cameron and Bell (*J. Phys. Chem.*, 1907, **11**, 363) and Carter and Hartshorne (*loc. cit.*) have shown that, even in saturated solutions, a relatively high ratio of phosphoric oxide to ferric oxide is present. This is apparent from Fig. 1 in which the values of P_2O_5/Fe_2O_3 calculated from the data given by these authors for the system at 25° are plotted against the corresponding phosphoric oxide concentrations. Some data obtained in the present work (see Table 3*a*) are also included. These confirm and extend some of the results obtained by the previous workers. The break in the curve at about 9% of phosphoric oxide corresponds to a change in the solid phase reported by Carter and Hartshorne, and the one at about 25% phosphoric oxide presumably corresponds to another change of solid phase.

Carter and Hartshorne (*loc. cit.*) have reported that metastable equilibria may be encountered in this system. This has been confirmed in the present work, the points close to the broken line in Fig. 1 indicating the compositions of solutions which were in metastable equilibrium after several weeks at 25°. At room temperature it was found that metastable equilibrium might persist for months. Apart from the experiments recorded in Table 4, the use of such solutions was avoided in the ion-exchange investigations in case precipitation of ferric phosphate on the resin occurred.

For the experiments with cation-exchange resins Permutit Zeo-Karb 225 was chosen as being a monofunctional, strongly acidic resin. It is of the sulphonated cross-linked polystyrene type with the sulphonic acid groups as the active exchange centres. Amberlite I.R.A. 400 was used for the anion-exchange experiments. It is a monofunctional strongly basic resin, supplied in the form of its chloride. For brevity, Z.K. will be used to represent the anion of Zeo-Karb 225 and Z.K.-H its hydrogen form. Similarly I.R.A. will be used to represent the cation of the anion-exchange resin and I.R.A.-Cl and I.R.A.-PO_4 its chloride and its phosphate form, respectively. (This should not be taken to imply that the phosphate ion is adsorbed as PO_4'''; in acid solutions it is apparently $H_2PO_4^-$ that is adsorbed.)

In a series of preliminary experiments, known volumes of solutions prepared from electrolytic iron (see p. 2322) were passed through columns of Z.K.-H. or I.R.A.-Cl. Although the solutions used at this stage were not saturated, the iron could be removed completely from the samples with the cation-exchange resin, but only at a low exchange equivalent (0·1 m.-equiv. of Fe/g. of resin; instead of the expected 2—3 m.-equiv./g.). The amounts adsorbed by the anion-exchange resin were still lower (about 0·03 m.-equiv./g. of resin). However, it was established by these experiments that iron was present as a complex anion. Further, by using suitable quantities of solution it was possible to remove all the iron from a sample by passing it through a column of Z.K.-H and then one of I.R.A.-Cl, or in the reverse direction. This showed that there was probably an equilibrium between ferric cations, or even complex cations, and anionic complexes containing iron, and that this was readily displaced either way. In an attempt to remove the iron from solution with the anion-exchange resin at a higher efficiency, further experiments were carried out with the resin in the phosphate form. It was found that the amounts of iron adsorbed by it were comparable with those retained by the cation-exchange resin. This observation is considered to add weight to the arguments advanced on p. 2317 for the need to examine this system in the absence of chloride ions. The results of this preliminary examination are summarised in Table 1.

The solutions used for these experiments tended to precipitate ferric phosphate on dilution, as would be expected from the rapid decrease of solubility of ferric phosphate in phosphoric acid with increasing dilution. To avoid the formation of a precipitate in the columns, it was necessary to adjust the level of liquid in the column to just below the top of the resin. The acid liberated by the exchange reaction then proved sufficient to prevent precipitation of the tertiary ferric phosphate. In one or two cases (not recorded in Table 1) where this precaution was not taken and a precipitate formed, it was immediately visible against the coloured resin and it also appeared as a suspension in the effluent from the column. It did not seem likely, therefore, that the retention of iron in the experiments just described was due to the formation of a precipitate in the columns, for it was not seen either there or in the effluent.

TABLE 1. *Column experiments with ferric phosphate solutions.*

Solution:			Columns: †		Fe, %:			Fe (m.-equiv.)/g. of resin on:	
					adsorbed on		in		
P_2O_5, M	Fe_2O_3, M	Ml. used	1st	2nd	Z.K.	I.R.A.	effluent	Z.K.	I.R.A.
0·16	0·001	25·00	Z.K.-H.	—	100	—	—	0·01	—
		50·00	Z.K.-H.	—	97	—	—	0·02	—
1·13	0·066	5·85	Z.K.-H.	Z.K.-H.	100	—	—	0·12	—
0·7 *	0·015	10·20	Z.K.-H.	IRA.-Cl	98	2	nil	0·09	0·002
1·8 *	0·067	5·10	Z.K.-H.	IRA.-Cl	96·5	3·5	nil	0·19	0·007
1·5 *	0·046	5·00	IRA.-Cl	Z.K.-H.	82	18	nil	0·12	0·026
1·13	0·066	5·01	IRA.-Cl	Z.K.-H.	79·6	18·4	2	0·16	0·038
1·8 *	0·067	5·00	IRA.-Cl	Z.K.-H.	82	17	1	0·16	0·034
1·13	0·066	6·00	IRA-PO_4	Z.K.-H.	30	70	—	0·07	0·17
		6·65	IRA-PO_4	IRA-PO_4	—	99	1	—	0·13
		5·00	IRA-PO_4	IRA-PO_4	—	100	—	—	0·099

* P_2O_5 in these solutions was estimated approximately from the quantity of phosphoric acid used in preparing them.

† The columns used held about 10 g. of resin (dry weight).

Tests showed that the cation-exchange resin adsorbed little or no phosphate with the iron and that the simple ferric ion was being adsorbed in preference to any complex cations which might be present. Consequently, the reaction with anion-exchange resins was studied.

In order to avoid the possibility of precipitation of the tertiary ferric phosphate arising from dilution of the solutions, this work was carried out with air-dried I.R.A.-PO_4. Weighed portions of this were left in contact with known volumes of saturated ferric phosphate solutions at room temperature for 1—8 weeks. The solution was then removed by filtration, and the resin transferred to a column and washed with water until the washings were neutral to methyl-orange. The column was then eluted with 2N-hydrochloric acid, at least 1 l. of acid being required to remove all the iron and phosphate from the resin, and the eluate was then analysed for iron and phosphate. The results obtained are shown in Table 2 and are plotted in Fig. 1. It can be seen that the molar ratio of phosphoric oxide to ferric oxide adsorbed varies with the concentration of phosphoric oxide in the solution in a manner similar to that shown by the ratio of those two substances present in solution, but the ratio of the amounts adsorbed on the resin is always less than the ratio of those present in saturated solutions. This suggests that there is present in these solutions a complex ferric phosphate anion which is stabilised by the presence of varying amounts of

TABLE 2. *Batch experiments with I.R.A. 400-phosphate (air-dried).*

Solution					Resin			
					Adsorbed:			
P_2O_5, %	Fe_2O_3, %	P_2O_5/Fe_2O_3	Vol. used, ml.	Weight used, g.	P_2O_5, mg.	Fe_2O_3, mg.	P_2O_5/Fe_2O_3	Fe (m.-equiv.)/g. of resin *
31·3	4·77	7·37	25	6·00	548	181	3·4	1·13
29·1	4·95	6·60	50	7·25	708	238	3·4	1·23
26·6	5·31	5·65	25	6·70	645	260	2·8	1·45
18·0	2·25	9·01	25	6·00	563	179	3·5	1·12
9·08	0·59	17·3	100	6·01	575	143	4·5	0·90
6·07	0·11	60·5	350	6·00	598	76	8·8	0·48

* Calc. by taking one-third of the atomic weight of iron as its equivalent weight.

excess of phosphoric acid. It appears also that the complex anion is more readily adsorbed by the anion-exchange resin than are the simple phosphate anions. The amount of excess of phosphoric acid needed to stabilise the complex is a minimum for solutions containing 25% of phosphoric oxide; for here the ratio of phosphoric oxide to ferric oxide has its minimum value, which is approximately 3. At this point the ratio of phosphoric oxide to ferric oxide adsorbed on the resin is also a minimum and again approximately 3. The inference is that at this concentration the solution contains a complex comprising three phosphate groups for each iron atom and that it is stabilised by a very small excess of phosphoric acid.

Fig. 1.

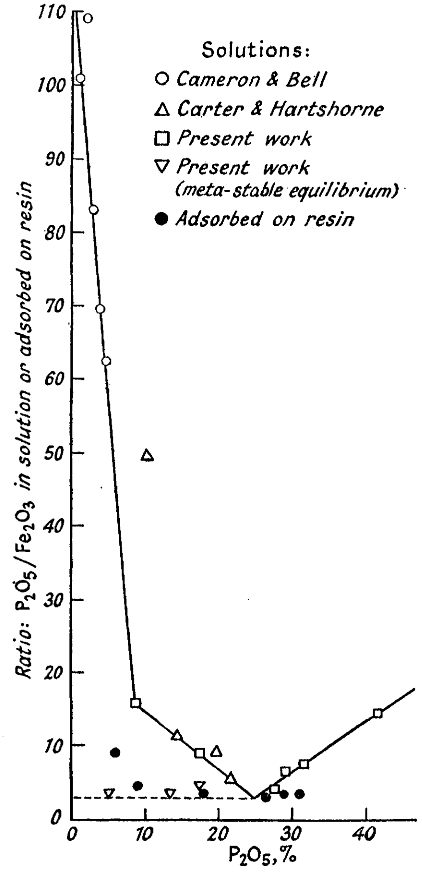
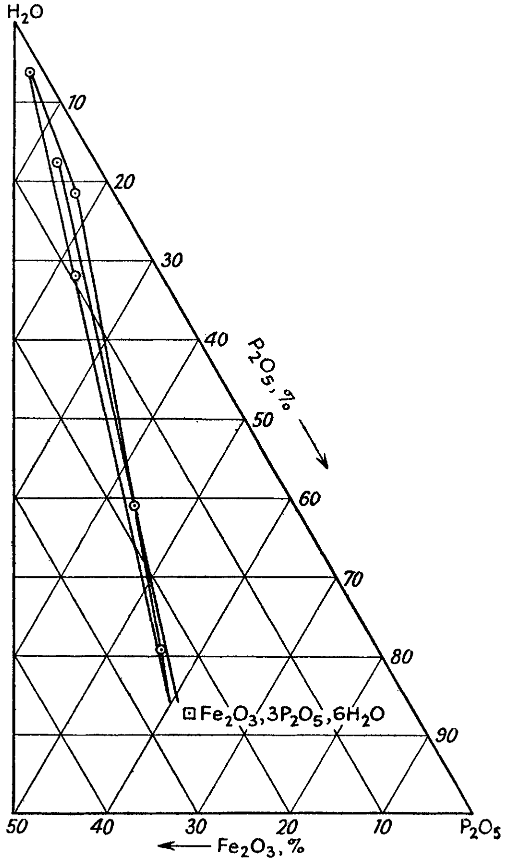


Fig. 2. Fe_2O_3–P_2O_5–H_2O *at* 25° (*metastable*).



A less likely interpretation, but one that must be considered, is that a complex containing two phosphate groups per iron atom is present in solution. At the minimum in the curve at 25% of phosphoric oxide, this complex would occur together with an equimolecular amount of phosphoric acid and these would be adsorbed by the resin in the same ratio. For this to happen, it would have to be the case that the complex and the simple phosphate ions were adsorbed with equal readiness by the resin. If this were true then with the more dilute solutions containing a higher ratio of phosphoric oxide to ferric oxide it would be expected that complex and simple ions would still be adsorbed in the same ratio as that in which they were present in solution. The results, however, do not support such a supposition.

The slight rise in the ratio of phosphoric oxide to ferric oxide adsorbed on the resin which occurs with solutions containing more than 25% of phosphoric oxide may be a result of increasing the concentration of phosphoric acid—and thus its competition in adsorption by the resin—or it may be due to the formation of complexes with increasing numbers of phosphate groups. With solutions containing less than 25% of phosphoric oxide, however, the increase in the ratio of phosphoric oxide to ferric oxide adsorbed is consequent on the increase in the ratio of these substances present in solution. The investigation was not extended to solutions containing less than 6% of phosphoric oxide because of the difficulty of obtaining them in a state of stable equilibrium. However, it was observed that with an unsaturated solution containing 2·24% of phosphoric oxide ($P_2O_5/Fe_2O_3 = 274$) all the iron present was removed from about 40 ml. of solution by 10 g. of air-dried I.R.A.-PO_4. The inference is justified, therefore, that, even at this dilution, anionic complexes are present.

The complex can apparently exist in a metastable state in the presence of a smaller excess of phosphoric acid than is required for stability, as indicated by the broken line in Fig. 1 (see Table 3*b*). The work of Cameron and Bell (*loc. cit.*) and of Carter and Hartshorne (*loc. cit.*) has shown that stable solutions containing less than 25% of phosphoric oxide are in equilibrium with a solid containing phosphoric oxide and ferric oxide in a molar ratio of 1 : 1. It may be inferred then that, once substitution of phosphate groups by aquo-groups starts, a stable state is not reached until the ratio of phosphoric oxide to ferric oxide becomes 1 : 1, at which stage solid tertiary phosphate is precipitated. As this hydrolysis proceeds, phosphoric acid is liberated and this in the end becomes sufficient to stabilise a small amount of complex remaining in solution.

TABLE 3.

(*a*) *Solutions in stable equilibrium.*

Solution:		
P_2O_5, %	Fe_2O_3, %	P_2O_5/Fe_2O_3
8·77	0·62	15·95
17·30	2·15	9·07
27·4	7·63	4·04
29·1	4·95	6·60
31·3	4·77	7·37
41·7	3·23	14·5

(*b*) *Solutions in metastable equilibrium.*

Solution:			Moist solid: *		
P_2O_5, %	Fe_2O_3, %	P_2O_5/Fe_2O_3	P_2O_5, %	Fe_2O_3, %	
5·13	1·53	3·78	22·83	9·52	I
13·64	4·26	3·60	43·7	17·8	
17·59	4·18	4·73	55·6	23·8	
3·97	0·87	5·13	9·41	6·14	II
7·87	1·65	5·37	24·1	21·0	
16·72	4·37	4·30	27·0	19·49	

* I, Solid phase apparently $Fe_2O_3,3P_2O_5,6H_2O$. II, Solid phase apparently $Fe_2O_3,P_2O_5,5H_2O$.

In Table 3*b* and in Fig. 2 data are presented relating to solutions and moist solid phases in metastable equilibrium at 25°. Because metastable states cannot be produced at will, they refer to only a few solutions, but they show that, in a region of the phase diagram where previous workers found the tertiary phosphate to be the stable solid phase, it is possible to obtain a metastable state where a substance apparently having the composition, $Fe_2O_3,3P_2O_5,6H_2O$, is the solid phase. It appears that this is the case only when the ratio of phosphoric oxide to ferric oxide in the solutions is not far from 3, otherwise the solid phase seems to be the tertiary phosphate, even for solutions in a state of metastable equilibrium. The circumstance that solutions containing phosphoric oxide and ferric oxide in a ratio slightly greater than 3 can exist in equilibrium, albeit only a metastable one, with a solid in which they are present in a ratio of 3 to 1, lends support to the view that the complex contains three phosphate groups per iron atom.

The fact that at 25% of phosphoric oxide the amount of phosphoric and ferric oxides adsorbed by the resin corresponds to a ratio of slightly less than 3 is probably not significant, since, for reasons given on p. 2323, the values of the ratios adsorbed shown in Table 2 are all 0·1—0·2 too low.

Although it must be accepted with reserve, evidence was obtained that in the solutions in metastable equilibrium a complex with fewer phosphate groups than 3 may occur. It came from two experiments with such a solution using I.R.A.-PO_4. The results, shown in Table 4, suggest that a complex containing 2 phosphate groups per iron atom may have been present together with one containing 3 phosphate groups. For reasons already given, these results—obtained as they were with a solution in metastable equilibrium—are not regarded as conclusive.

This investigation thus indicates that there is present in ferric phosphate solutions a complex containing three phosphate groups per iron atom. Some support for this conclusion is provided by the examination of some metastable states of the ferric phosphate system. The phosphate group presumably acts as a bidentate group in the complex, but, at this stage, it is not certain whether it is the HPO_4'' or the PO_4''' group which is present. The complex may, therefore, be either $H_3[Fe(HPO_4)_3]$ or $H_6[Fe(PO_4)_3]$.

TABLE 4. *Experiments with solutions in metastable equilibrium.*

Solution :				Resin :			
			Vol.	Weight	Adsorbed :		
P_2O_5, %	Fe_2O_3, %	P_2O_5/Fe_2O_3	used, ml.	used, g.	P_2O_5, mg.	Fe_2O_3, mg.	P_2O_5/Fe_2O_3
6·23	0·88	7·95	200	6·00	581	303	2·15
			50	6·00	583	273	2·40

EXPERIMENTAL

Preparation of Solutions.—The methods used were : (*a*) Dissolving the tertiary phosphate or ferric hydroxide in phosphoric acid (7M or stronger) to obtain a saturated solution at about 80° and then diluting this to the required concentration. (*b*) Dissolving electrolytic iron in phosphoric acid of the required concentration, oxidising the solution so obtained with hydrogen peroxide (80-vol.) and either allowing the excess of hydrogen peroxide to decompose at 25° or hastening this process by short warming on a water-bath. (Care had to be taken with solutions containing less than 25% of P_2O_5 not to heat them for too long, since—as a result of the negative temperature coefficient of solubility—a solid separated on overheating and it redissolved only slowly at lower temperatures.) The solutions were then allowed to come to equilibrium with a solid phase before use. The more dilute solutions were colourless, the others lilac-coloured.

Preparation of Ferric Hydroxide.—This was obtained by precipitation from ferric alum solution with ammonia and was washed by decantation: each fresh batch of wash water was thoroughly mixed with the suspended hydroxide by several hours' stirring before it was allowed to settle. When the washings were free from sulphate, the hydroxide was filtered off, washed, and left to dry in the air. Some hydroxide was lost in washing, but the product appeared to be pure.

Preparation of Ferric Phosphate.—To a solution of ferric alum (25 g.) in dilute sulphuric acid (12 ml. of 6N-acid in 300 ml. of water) a solution of sodium dihydrogen phosphate (25 g. of dihydrate in 400 ml. of water) was added; on heating, a white voluminous precipitate formed and this gradually became more granular. After several hours the suspension was allowed to cool, the liquid layer was decanted and replaced by a solution of 1 ml. of concentrated phosphoric acid in 500 ml. of water, and the suspension heated on a water-bath for 5—6 hours. The supernatant liquid was decanted, and the process repeated two or three times, but with water in place of acid. The precipitate was then filtered off, washed, and air-dried. It was free from sodium [Found: Fe_2O_3, 40·27; P_2O_5 (by diff.), 35·94; H_2O 23·79. Calc. for $Fe_2O_3,P_2O_5,5\frac{1}{4}H_2O$: Fe_2O_3, 40·30; P_2O_5, 35·82; H_2O, 23·87%]. It was assumed to be the compound, $FePO_4,2\frac{1}{2}H_2O$, described in the literature, but incompletely dried.

Materials.—With the exception of the electrolytic iron, analytical-grade reagents were used in preparing all compounds and solutions. The commercial resins (see p. 2318) were freed from " fines " and given a preliminary treatment with 2N-hydrochloric acid. To convert the anion-exchange resin into the phosphate form, 25 g. of resin in a column were treated with sodium dihydrogen phosphate solution (100 g. of dihydrate/l.) until the effluent was free from chloride. The resin was then washed with water until the washings were neutral to methyl-orange (pH 5 approx.).

Apparatus.—The containers used were Monax or Pyrex boiling-tubes or flasks closed with rubber bungs. The thermostat for the phase-diagram studies was kept at 25° ± 0·1°.

The columns used for the ion-exchange experiments were of conventional design and made of hard glass with a grade 2 sintered disc sealed in position. Two sizes of column were used, one capable of holding 10 g., and the other about 25 g. of resin (dry weight).

Procedure.—In the analysis of solutions, samples were taken by pipette and were transferred to weighing bottles which were immediately stoppered. After the samples had been weighed, a few ml. of concentrated hydrochloric acid were added (to prevent precipitation on dilution) and the solutions diluted to known volume, aliquot portions being taken for analysis. The moist solid phases were separated as far as possible from the solutions by filtration. They were then weighed, dissolved in hydrochloric acid, and treated in the same way as the solutions.

In the column experiments with the ion-exchange resins, the solutions were added dropwise from a tap-funnel or burette and were followed in each case by at least 1 l. of water. The materials adsorbed by the resin were removed by elution with 2N-hydrochloric acid, 1—1½ l. being used. After the eluted column had been washed with water until the washings were neutral to methyl-orange, the resins were ready for further use.

In the batch experiments, it was found that the composition of solutions in contact with resins varied for the first 3 days, but then remained constant. In practice a longer time was allowed before filtering off the solution and washing the resin carefully with small portions of water. After being transferred to a column, the resin was washed until the washings were neutral to methyl-orange and then eluted with 2N-hydrochloric acid. The eluate (approx. 1¼ l.) was evaporated to about 25 ml., diluted to 200 ml., and passed through a column of Z.K.-H (25 g.) to remove the iron. It was followed by 1 l. of water, the phosphate being determined in the combined effluent and washings. The column was eluted with 2N-hydrochloric acid, the iron being determined in the effluent.

Analytical Methods.—Iron was determined by titration with standard potassium dichromate solution (approx. N/20) after reduction with stannous chloride. Diphenylamine was used as the indicator.

Phosphate was determined by titration with standard bismuth oxyperchlorate solution (approx. M/20) (Salmon and Terrey, *J.*, 1950, 2813). Iron was first removed by percolating the solution through a column of Z.K.-H. The hydrochloric acid added to the samples interfered in the titration with bismuth oxyperchlorate and was first removed by evaporating the effluent nearly to dryness and then heating it on a steam-bath until no more acid fumes were evolved.

In the separation of iron in this way from the eluates from the batch experiments with I.R.A.-PO_4, it was found that some of the phosphoric acid was retained by the Z.K.-H. column and was eluted from it together with the iron on treatment with 2N-hydrochloric acid. The amount involved was determined by evaporating an aliquot portion of the eluate to dryness, dissolving the residue in concentrated nitric acid (25 ml.), boiling the solution to expel brown fumes, and diluting it with water before precipitation as ammonium phosphomolybdate. The amount of phosphate held by the Zeo-Karb seemed to vary with the amount of iron adsorbed, but corresponded to approximately 3% of the phosphoric acid present in the sample. As a determination was not made in every case, the values in Table 2 have not been corrected to allow for this and the values of the ratio in the eighth column are consequently about 0·1 too low.

In the analysis of the solutions and moist solid phases, where much smaller quantities of iron were being separated, no significant retention of phosphate by the Zeo-Karb resin was observed. The effluent and washings from the Zeo-Karb columns were also tested for iron but the amount present was negligible.

Although the analytical-grade hydrochloric acid used in making the 2N-acid contained but little iron, the large volumes of it used in the course of the batch experiments meant that some iron was introduced in this way. A blank experiment showed that about 5 mg. of iron could be thus introduced. The amounts found for the iron adsorbed are, as a result, about 2% too high and the values of the ratio in the eighth column of Table 2 are consequently about 0·1 too small. It follows that the deviation of the lowest value from 3 is not significant.

The water present in the tertiary phosphate was determined by the loss on heating it to constant weight at dull red heat.

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