XLVII.—*The System Ferrous Oxide–Phosphoric Acid–Water and Some of its Oxidation Products.*

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IN addition to the promised work (J., 1923, **123**, 2223) on the ferrous phosphates, this paper describes a study of the oxidation of some of the ferrous-phase complexes, which has thrown fresh light on the composition of the neutral ferric phosphates.

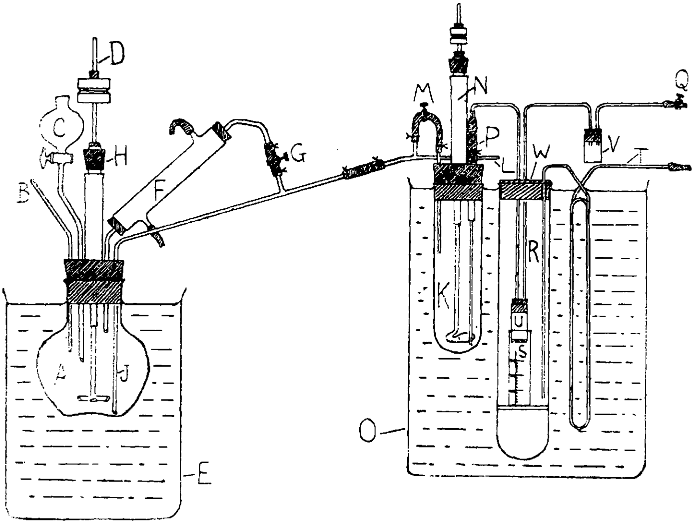
The following ferrous phosphates are described in the literature: $Fe_3(PO_4)_2,8H_2O$, or $3FeO,P_2O_5,8H_2O$, occurs in nature as *vivianite* and has been prepared by Becquerel (*Ann. Chim. Phys.*, 1833, **54**, 149), Debray (*ibid.*, 1861, **61**, 437), Horsford (*Sitzungsber. Akad. Wiss. Wien*, 1873, **67**, 466), and Evans (*Pharm. J.*, 1897, **4**, 141). $Fe_3(PO_4)_2,6H_2O$, or $3FeO,P_2O_5,6H_2O$, has been obtained by Gautier (*Compt. rend.*, 1893, **116**, 1491). Two acid phosphates are described, *viz.*, $FeHPO_4,H_2O$, or $2FeO,P_2O_5,3H_2O$, by Debray (*loc. cit.*), and $Fe(H_2PO_4)_2,2H_2O$, or $FeO,P_2O_5,4H_2O$, by Erlenmeyer (*Annalen*, 1878, **194**, 176). Kunz-Krause (*Ber. Deut. pharm. Ges.*, 1923, **33**, 20) describes a substance, containing ferrous and ferric iron and phosphoric acid, which is found in certain arable soils. This he assumes to be a basic ferrous ferric phosphate.

EXPERIMENTAL.

As in the case of the ferric phosphates (*loc. cit.*), the system was studied at 70°. The equilibrium mixtures were prepared by dissolving excess of Swedish iron wire (99·75% Fe) in solutions of phosphoric acid, obtained from the same source as that used in the ferric phosphate investigation. This operation, the subsequent stirring to attain equilibrium, and the collection of the liquid and solid phases were performed in an atmosphere of carbon dioxide in an apparatus (Fig. 1) in which the rubber stoppers were coated with paraffin wax or collodion and the connexions were made with thick-walled pressure tubing carefully wired on. The iron wire, in lengths of about ½ inch, was placed in the flask A, and the air in the apparatus was then displaced by passing carbon dioxide, admitted through the tube B, for about 2 hours, care being taken to clear all " pockets " such as stirrer bearings. The carbon dioxide was obtained from ordinary commercial cylinders and in some cases was sufficiently pure to be used directly, but in others the gas was passed through chromous chloride solution to remove the small quantity of oxygen present, then through sodium bicarbonate solution to remove hydrochloric acid, and finally through strong sulphuric acid. (One sample of chromous chloride solution of about 250—300 c.c. was required for a series of experiments lasting several months and during this time no alteration in the characteristic blue colour of the solution was observed. We attribute this to the fact that the solution was kept in contact with amalgamated zinc, which appears effectively to regenerate the chromous chloride after it has been oxidised, hydrochloric acid, presumably, being formed.)

Phosphoric acid solution of the required strength, freshly boiled and still hot, was run into the flask through the tap-funnel C. The mixture was then stirred with the mercury-sealed stirrer, D, until sufficient solid phase had formed, the flask being meanwhile maintained at approximately 70° by means of the water-bath, E, and undue evaporation of water prevented by the condenser, F. The stirrer was then stopped and its bearing sealed by the rubber stopper, H, to withstand pressure. By closing the clip, G, and admitting more carbon dioxide to the flask, a portion of the mixture was forced up the tube J and into the solubility tube, K, which was one of a series of four, the remainder (not shown) being connected, in a manner similar to K, to an extension of the tube L. By suitable adjustment of screw clips (*e.g.*, M) the mixture could be admitted to one or other of these solubility tubes, the displaced carbon dioxide escaping through the mercury seals, N, etc. The tubes were supported in the thermostat, O, fitted with a glass window and maintained at 70° ± 0·1° by an ordinary gas-regulator.

FIG. 1.



A suitable quantity of mixture having been transferred to K, the composition of the remainder in A was altered by the addition of a few c.c. of either water or syrupy acid and the next solubility tube was filled, and so on. Four mixtures of slightly different compositions were thus obtained from one sample of iron. The object in not dissolving the iron directly in the solubility tubes was to avoid the excessive frothing which occurred when this was attempted. The flask A was of such a shape and size that the froth could not rise : further the method ensured that the mixtures were free from undissolved iron which might have interfered with the collection of phase samples and would probably have rendered the attainment of equilibrium slow and uncertain.

The mixtures were stirred for at least a week, usually longer, and from the regularity of the results it is inferred that equilibrium had then been attained. In deciding the time allowed for stirring we had to be guided by our experience of the ferric system, since it would have been impracticable, on account of the risk of oxidation, to open the solubility tubes for the purpose of withdrawing samples for trial analyses. During the stirring the pressure of the carbon dioxide in the apparatus was maintained slightly above atmospheric in order to minimise the effect of leaks (great care, however, was taken to exclude these) and diffusion through the rubber connexions, and to counterbalance any reduction in pressure due to cooling caused by a fall in level of the thermostat water.

The apparatus for collecting the phase samples was essentially the same as that used in collecting the moist solid phase in the ferric system (*loc. cit.*), with the addition of arrangements for maintaining an atmosphere of carbon dioxide in and around the filter. The figure shows it connected to the solubility tube by means of the collecting tube P, which normally was closed with a piece of glass rod. Before this connexion was made, the collecting apparatus was cleared of air by a current of carbon dioxide admitted at Q, and the jacket, R, containing the weighing-bottle, S, was also cleared, by gas entering through the tube, T, the coiled portion of which, immersed in the thermostat, served to heat the gas and thus prevent cooling of the jacket. Connexion was then made as quickly as possible, the final arrangement being shown in the figure. By suitable adjustment of the gas pressure in different parts of the apparatus the mixture of liquid and solid phases was then blown over into the weighed filter, U (any overflow being caught in the trap, V), and was filtered. The liquid phase was caught in the weighing-bottle, S. During filtration an atmosphere of carbon dioxide was maintained in R by means of T, entry of air being minimised by the loose-fitting cork cover, W.

The liquid and moist solid phases were analysed by the methods used in the ferric system. In calculating the percentage of ferrous oxide, it was assumed that the whole of the iron was present in this state, although actually it was always found that the mixtures were oxidised to some extent, usually less than 1%. This point is discussed in the following section.

Analyses of the solid phases in the dry state were also made. The drying was accomplished in some cases by washing with dry ether alone, in an atmosphere of carbon dioxide. The apparatus used consisted of a filter flask in the neck of which a wide straight adapter and a tube for admitting carbon dioxide were supported by means of a rubber stopper. The side tube of the flask carried a mercury bubbler. A filter was made up in the adapter by means of two porcelain filter plates with a layer of asbestos between them, and the neck of the adapter was fitted with a rubber stopper carrying a tube for admitting carbon dioxide, a dropping-funnel, and a capillary tube which could be closed by a screw clip fitted to a rubber extension. The air was removed from the filter flask by means of carbon dioxide and with a steady stream of this passing through the filter, the moist solid was rapidly transferred to the adapter, the stopper carrying the dropping-funnel, etc., being removed as long as was necessary to accomplish this. The air was then quickly blown out of the adapter by carbon dioxide, the capillary tube serving as outlet. This was then closed and by increasing the pressure of the carbon dioxide as much liquid as possible was expressed from the moist solid. By alternately releasing and raising the pressure by operating the clip on the capillary tube, ether could be admitted from the dropping-funnel and forced through the solid.

In cases where ether could not readily be made to pass through the solid the following procedure was adopted. The solid was shaken for a few moments in a large weighing-bottle with water, containing two or three drops of concentrated hydrochloric acid (to remove any crust of ferric salt), which was then decanted and the process repeated with two or three washings of water, alcohol, and dry ether, respectively. The solid was finally dried in a stream of carbon dioxide.

Results.

The results are in Table I and are plotted by the triangular method in Fig. 2. Analyses of the dry solids are in Table II. In the second column of Table I figures are given for the percentage of iron present in the ferric state in some of the mixtures. This was determined by rapidly dissolving the contents of the overflow trap V (Fig. I) in water acidified with hydrochloric acid and

TABLE I.

Mixture.	% oxidation.	Liquid phase.			Moist solid phase.		Solid phase.
		$d_4^{15-20°}$.	% FeO.	% P_2O_5.	% FeO.	% P_2O_5.	
1	1·2	1·08	2·76	7·38	—	—	$2FeO,P_2O_5,5H_2O$.
2	—	1·16	4·38	12·06	34·9	35·51	
3	—	1·22	5·53	14·46	10·5	17·84	
4	1·6	1·20	5·48	14·96	35·9	36·0	
5	5·1	1·24	5·54	15·1	17·9	24·1	
6	—	1·31	7·71	21·6	—	—	$2FeO,P_2O_5,3H_2O$. Well-formed crystals, average length 0·1 mm.
7	0·84	1·39	9·18	25·65	—	—	
8	—	1·43	9·88	28·25	—	—	
9	—	1·53	10·99	32·78	—	—	
10	—	1·60	11·25	37·20	19·8	38·07	
11	—	1·60	11·29	37·21	21·3	39·13	
12	—	—	9·12	24·29	24·3	32·17	$2FeO,P_2O_5,3H_2O$. Amorphous particles, average length 0·014 mm.
13	—	1·42	10·1	27·20	21·9	32·47	
14	—	1·44	10·6	29·05	23·6	34·01	
15	0·87	1·45	10·6	29·46	23·2	33·39	
16	0·62	1·54	11·3	32·87	20·7	34·61	
17	0·92	1·55	11·5	33·99	26·3	37·81	
18	—	—	11·8	35·43	13·8	35·81	
19	2·75	1·60	11·9	36·99	—	—	
20	0·7	1·58	10·5	38·86	17·8	44·63	$FeO,P_2O_5,4H_2O$.
21	—	1·60	8·77	41·52	18·8	46·84	
22	—	—	7·38	42·88	—	—	
23	—	1·61	6·29	46·61	16·2	48·10	
24	—	1·63	4·87	50·49	12·7	50·38	
25	—	1·63	4·01	52·02	18·2	50·52	
26	4—6	1·71	3·15	57·51	15·2	53·12	

TABLE II.

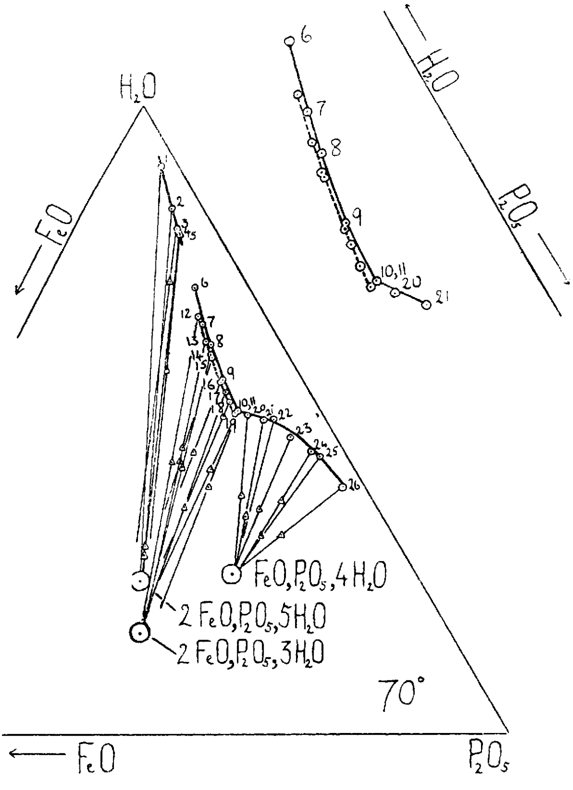
Analysis of Dry Solid Phases.

Mixture.	Found.		Formula assigned.	Theoretical composition.	
	% FeO.	% P_2O_5.		% FeO.	% P_2O_5.
Specially prepared	38·0	37·8 38·0	$2FeO,P_2O_5,5H_2O$	38·3	37·8
9	41·6	41·7 40·7	$2FeO,P_2O_5,3H_2O$	42·4	41·8
22	24·8	49·5 49·7	$FeO,P_2O_5,4H_2O$	25·2	49·65

titrating a portion of the solution with potassium dichromate directly and then titrating another equal portion, after reduction by stannous chloride. The method gave only a very approximate value, since the first stages of oxidation are probably confined to the liquid phase (in the four-component system $FeO–Fe_2O_3–P_2O_5–H_2O$ the ferrous salts must have some region of existence as solid phases in the presence of ferric iron) and the samples taken consisted of both solid and liquid phases in varying relative amounts.

Moreover, an appreciable degree of oxidation probably occurred before the first titration could be completed. The figures were useful, however, as a rough test of the inertness of the atmosphere maintained over the mixtures during stirring. The high values given by mixtures 5 and 26 were due to the use of carbon dioxide which was subsequently found to contain 1% of oxygen. As already stated, the oxidation was neglected when the ferrous oxide percentages were being calculated, since any attempt to determine the oxidation in liquid and moist solid phases separately, and make the necessary allowances, would have increased the already great difficulties in collecting the phase samples, besides being fraught with uncertainty as to whether the results would really represent the condition before the solubility tubes were opened. As justification for our procedure we may point to the regularity with which most of the solubility points lie on smooth curves and to the evidence afforded by the conjugation lines for the composition

Fig. 2.



of the solid phases, this evidence being confirmed by analysis of the dry solids.

The third column in Table I gives the densities of the liquid phases. The values were obtained by comparing the weights of the samples with their volumes at room temperature, estimated to 0·25 c.c. by the graduations on the side of the weighing-bottle S (Fig. 1). Since the average volume of a sample was near 20 c.c., the figures are accurate to about 1 part in 80.

With regard to the solid phases, within the range of acid concentrations studied, no neutral salt such as vivianite exists. It probably has a small range of existence in the region below the point corresponding to 7·38% P_2O_5 of mixture 1, but we have found it impossible to study this region on account of the increased susceptibility to oxidation which occurs as the acid concentration diminishes. Starting with the dilute-acid region, the first solid phase found, $2FeO,P_2O_5,5H_2O$, or $FeHPO_4,2H_2O$, has, as far as we are aware, not been described before. Its composition is confirmed by the analysis of the dry solid (Table II) and its crystalline form is shown in the photomicrograph reproduced in Fig. 3. We are indebted to Dr. Leonard Hawkes, Head of the Geology Department at Bedford College, for the following crytallographic analysis under the microscope. Biaxial; positive; axial angle $2V_\gamma =$ *ca.* 60—70°; dispersion of optical axis $\rho > \nu$ (?); optical axial plane parallel to the length axis of the prism. Examination was rendered difficult on account of the elongated habit and consequent tendency to settle on the slide in one position only.

The next solid phase, $2FeO,P_2O_5,3H_2O$ or $FeHPO_4,H_2O$, was described by Debray (*loc. cit.*), but doubt was subsequently cast on this author's work by Erlenmeyer (*loc. cit.*). We, however, have confirmed its existence both by the graphical method and by analysis of the dry solid (Table II). The figures are not so satisfactory as the analyses of the other dry solids owing to the very small amount of material available, but they are sufficiently conclusive. We have obtained it in two distinct forms which have slightly different solubility curves. This is shown clearly in Fig. 2, where this portion of the isotherm is drawn separately on an enlarged scale. The form showing the greater solubility is very finely divided and the particles are almost destitute of crystalline form while showing a characteristic elongated shape. A specimen of those in equilibrium with mixture 16 is shown in Fig. 4. The average length of the particles in this photomicrograph, which may be taken as representative of the whole series, is estimated to be 0·014 mm. Evidence for the composition of this solid is based solely on the conjugation lines, since all efforts to dry the solid failed, no doubt on account of its extremely fine state of division.

The form showing the lower solubility is definitely crystalline. The type of the crystals in equilibrium with mixtures 9, 10, and 11 is shown in Fig. 5. The crystals are plates having, usually, six sides. The average diameter of those in the figure, measured in the direction of greatest length, is about 0·1 mm. Evidence for the composition of this form is based chiefly on the analysis of the dried solid in equilibrium with mixture 9 (Table II), the evidence of the conjugation lines from mixtures 10 and 11, which apparently lie at an invariant point, being inconclusive.

Mixtures 6, 7, and 8 gave a crystalline solid phase which was quite unlike any of the others in appearance. Unfortunately in no case was there sufficient material for analysis. The crystals are shown in Fig. 6. From the position of the liquid-phase points on the diagram (Fig. 2) we have concluded that it is another habit of the crystalline compound $2FeO,P_2O_5,3H_2O$ and accordingly have included the analytical figures in that section of Table I. The average length of the crystals (Fig. 6) was about 0·1 mm.

It appeared at first that the deposition of one form or the other was fortuitous. Subsequent perusal of the experimental notes showed, however, that in those cases where a suitable mixture (*i.e.*, one having convenient proportions of solid and liquid phases) was obtained at once in the reaction flask A (Fig. 1) and was transferred immediately to the solubility tubes, the more soluble form was obtained, whereas if further additions of iron or phosphoric acid solution were necessary, or if during the dissolution of the iron the temperature was raised or lowered (as was sometimes done to break up cakes of solid formed over-night in the reaction flask, or for other practical reasons), then the less soluble crystalline form resulted. Qualitative observations have shown that the salt has a very small temperature coefficient of solubility; moreover, its solubility is not greatly altered by varying the concentration of acid (see Fig. 2). If we assume that the molecules aggregate much more rapidly than they subsequently arrange themselves to form crystals, it is clear that the form first deposited will be an irregular aggregate, *i.e.*, an amorphous or quasi-amorphous solid. Moreover, since the solubility is scarcely affected by temperature and concentration, the aggregates may remain undisturbed for a long period unless these conditions are altered considerably. The aggregated form has more free energy than the crystalline variety and will be metastable and more soluble. The theory that the difference in solubility is connected in any way with the difference in particle size (given above) may be dismissed, since the particles were probably too large for this factor to be operative (compare Hulett, *Z. physikal. Chem.*, 1901, **37**, 385, who found differences in the solubility of particles of diameter 0·002 mm. and less) and in any case the mixtures were stirred sufficiently long (8, 10, and 33 days) for the larger particles to grow at the expense of any small enough to give an abnormal solubility.

The solid phase in the mixtures richest in acid was the compound $FeO,P_2O_5,4H_2O$ or $Fe(H_2PO_4)_2,2H_2O$, described by Erlenmeyer (*loc. cit.*). Its composition is amply confirmed both by the conjugation lines (Fig. 2) and by analysis of the solid in equilibrium with mixture 22 (Table II). Typical crystals are shown in Figs. 7 and 8. It has a positive temperature coefficient and crystallises spontaneously within 24 hours from appropriate liquid phases which are allowed to cool to room temperature.

The colour of the liquid phases throughout the isotherm was the pale green characteristic of the ferrous ion. The solids were also pale green. The formation of complexes, which takes place in the ferric system, does not therefore appear to occur here.

Oxidation of the Mixtures.

It has already been stated that the mixtures poor in acid were particularly susceptible to oxidation. This showed itself in the formation of reddish-brown crystals which were deposited to a greater or less extent after the mixtures had been stirred for some days, and appeared to exist in stable contact with the ferrous phosphate already present. In mixture 1, the solid phase consisted almost entirely of these crystals and therefore it was obviously useless for the purpose of the ferrous isotherm to analyse the moist solid. It was, however, of interest to find out the composition of the crystals and it was fortunately found possible to separate them from admixed ferrous phosphate by the brief action of dilute hydrochloric acid. This was discovered by watching the behaviour of the mixture under the microscope, when, on adding a drop of hydrochloric acid, the ferrous phosphate dissolved almost immediately while the brown crystals appeared to be unaltered. The solid was therefore washed, by shaking with dilute hydrochloric acid for some minutes, transferred to a filter, and washed under pressure successively with a little more dilute acid, water, alcohol, and dry ether. A little of the solid, immediately dissolved in hydrochloric acid, gave only a very faint response to the test for ferrous iron. It was therefore not a ferroso-ferric phosphate. It gave a strong ferric reaction. Analysis of the remainder gave Fe_2O_3, 42·2; P_2O_5, 37·7. $Fe_2O_3,P_2O_5,4H_2O$ requires Fe_2O_3, 42·8; P_2O_5, 38·0%, and $Fe_2O_3,P_2O_5,4{\cdot}25H_2O$ requires Fe_2O_3, 42·3;

P_2O_5, 37·5%. The result thus agrees very closely with the latter formula, but we consider that, failing further evidence, it is better to regard it as incompletely dried $Fe_2O_3,P_2O_5,4H_2O$.

The naturally occurring strengite has this composition, and Erlenmeyer (*loc. cit.*) claims to have prepared a neutral phosphate of this composition; his analytical figures, however, are not very conclusive, as we pointed out in our earlier paper. Crystals of our compound are shown, as dark, rectangular prisms, side by side with ferrous phosphate in Figs. 3 and 6.

Since in the ferric system we had not observed a solid which resembled these brownish-red crystals in appearance, it seemed evident that they were only stable in the presence of ferrous iron and that if oxidation were completed, the solid would change. To test this point, a mixture was prepared in the region of existence of $2FeO,P_2O_5,5H_2O$ and was stirred at 70° in a solubility tube, the bearing of which was not sealed by mercury. From time to time the solid phase was examined microscopically, and the liquid tested for ferrous iron. Water was added as required to make up for loss due to evaporation through the stirrer bearing. The brown ferric salt was present from the first, and after 8 days constituted the whole of the solid phase, all the greenish-white, ferrous phosphate having disappeared. The liquid phase, however, still showed a strong ferrous reaction. After a further 8 or 9 days the brown colour of the solid had given place to a pale pink shade, resembling that of the ferric phosphates encountered in our previous work. Under the microscope, the solid was seen to be very much broken but definitely crystalline, many of the crystals having a characteristic kite-like shape. These are shown in Fig. 9, where a well-formed specimen will be seen in the middle of the picture. At this stage the liquid phase still showed a fairly strong ferrous reaction. Stirring was continued for another week without any change occurring in the appearance of the solid, but the liquid phase now gave a very weak ferrous reaction. The mixture was then left unstirred for another fortnight; it was then completely oxidised. It was stirred for a few hours to ensure equilibrium and the liquid and the solid (dry) were analysed. The liquid contained a trace of Fe_2O_3 and 7·09% of P_2O_5. The solubility curve of the ferric phosphates (*loc. cit.*, p. 2230) shows that the quantity of Fe_2O_3 corresponding to 7·09% P_2O_5 is measurable, being about 0·1%. This slight difference in solubility may, however, be attributed to the solid in that case having been amorphous, whereas here it was crystalline, and therefore we conclude that the same compound was concerned in both cases. The reason for obtaining the crystalline form by oxidation of a ferrous mixture

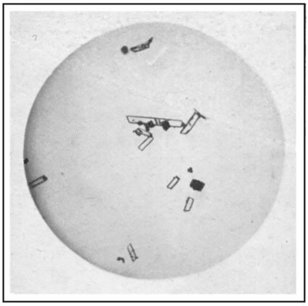


FIG. 3.—$2FeO,P_2O_5,5H_2O$ and β-$Fe_2O_3,P_2O_5,4H_2O$ (short dark prisms). ×10

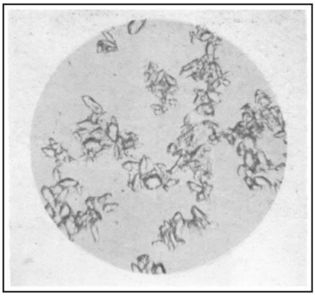


FIG. 4.—$2FeO,P_2O_5,3H_2O$ ("amorphous") × 160.

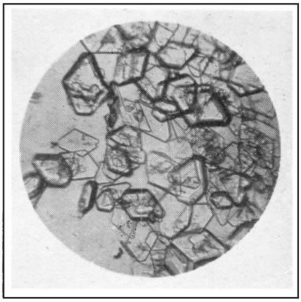


FIG. 5.—$2FeO,P_2O_5,3H_2O$ (crystalline). × 57.

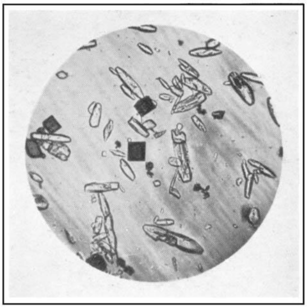


FIG. 6.—$2FeO,P_2O_5,3H_2O$ (crystalline) and β-$Fe_2O_3,P_2O_5,4H_2O$ (short dark prisms). × 50.

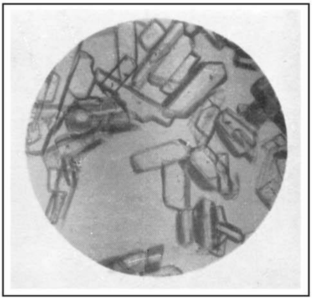


FIG. 7.—$FeO,P_2O_5,4H_2O$. × 25-50.

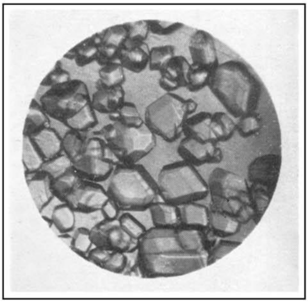


FIG. 8.—$FeO,P_2O_5,4H_2O$. × 43.

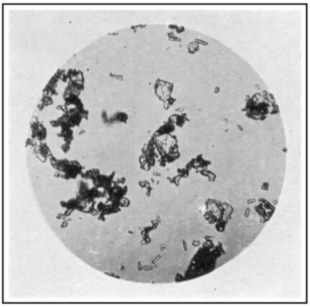


FIG. 9.—α-Fe_2O_3 $P_2O_5,4H_2O$. × 90

[*To face page* 372.]

probably lies in the gradual decrease in solubility which occurs during the process or in other factors inherent in it, which affect the velocity of crystallisation as opposed to aggregation and are evidently absent or suppressed when ferric oxide is treated with dilute phosphoric acid.

Analysis of the solid phase gave Fe_2O_3, 42·25; P_2O_5, 37·5, 37·6%, which, within the probable limits of experimental error, is the same as the composition found for the brown crystals. There are thus two neutral ferric phosphates having the composition $Fe_2O_3,P_2O_5,4H_2O$ in the four-component system Fe_2O_3–FeO–P_2O_5–H_2O at 70°. We will call the pink the α-form and the brown the β-form. Under the conditions studied, the α-form is stable in the absence, or in low concentrations, of ferrous iron, whilst the β-form exists in the presence of medium to quite high concentrations: indeed, judging from the readiness with which it crystallises from ferrous mixtures, in spite of all efforts to maintain an inert atmosphere, it may be inferred that in this region the range of existence of solutions in equilibrium with a ferrous salt only is very limited.

The difference between the α- and the β-salt may be explained in a similar way to that applied in the case of the neutral ferric phosphates at 25° (*loc. cit.*). As we mentioned there, the work of Weinland and Ensgraber showed that the pink ferric phosphates were probably complex ferri-phosphates. Thus we may suppose that the pink α-form has the constitution $[Fe(PO_4)_2]Fe,4H_2O$, while the brown β-salt is a true ferric phosphate, $FePO_4,2H_2O$. Support for the latter supposition is given by the colour changes which ferrous phosphate solutions undergo on oxidation: the original green colour changes to brown and finally to pink. The intermediate brown colour may well be due to the ferric ion, and it is the β-form which can exist at this stage.

It is now seen that we were in error in our earlier work in attributing five molecules of water to the solid phase in equilibrium with the weakly acid solution at 70°. That such a hydrate does exist appears to have been confirmed by Weinland and Ensgraber, and in our own work at 25° there seems to be little doubt that it was present. At 70°, however, the α-salt with four molecules of water is stable, at least in the region in which the above oxidation experiment terminated.

Summary.

1. The system FeO–P_2O_5–H_2O has been studied at 70°, between the concentrations 7·38 and 57·51% P_2O_5. Within this range the stable solid phases are the acid salts $2FeO,P_2O_5,5H_2O$, $2FeO,P_2O_5,3H_2O$, and $FeO,P_2O_5,4H_2O$, the first of which has, as far as is known, not been described before.

2. By the oxidation of phases poor in acid, two neutral ferric phosphates, both having the composition $Fe_2O_3,P_2O_5,4H_2O$, are deposited. The brown β-form exists in contact with liquid phases having high to medium concentrations of ferrous iron; at lower concentrations, the pink α-form becomes stable.

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