3 Published Papers

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Ph.D

A Thesis presented to the University of London for the Degree
of Doctor of Philosophy
by
Norman Holt Hartshorne.

ABSTRACT.

(I) The System Ferrous Oxide-Phosphoric Acid-Water and some of its Oxidation Products.

The existence of the monohydrogen ferrous phosphate $Fe(HPO_4),H_2O$ (or $2FeO,P_2O_5,3H_2O$) has been confirmed. This compound was described by Debray but subsequently Erlenmeyer cast doubt on Debray's results. The compound has been obtained in two forms, viz. "amorphous" and crystalline, the latter showing a decidedly lower solubility. In addition a dihydrate $Fe(HPO_4),2H_2O$ (or $2FeO,P_2O_5,5H_2O$) has been shown to exist. The dihydrogen phosphate $Fe(H_2PO_4)_2,2H_2O$ (or $FeO,P_2O_5,4H_2O$) described by Erlenmeyer has been confirmed. It is thought that the ferrous phosphates are not complex.

By the oxidation of phase mixtures poor in acid a red-brown ferric phosphate $\beta Fe_2O_3,P_2O_5,4H_2O$ is deposited, which is only stable when ferrous iron is present in the liquid phase (at 70°). By completing the oxidation the substance changes both in crystalline form and colour (to pink) to a solid having the same empirical composition $\alpha Fe_2O_3,P_2O_5,4H_2O$. It is thought

that the latter is a complex ferri-phosphate, whilst the former is a true ferric phosphate.

(II) An Apparatus for the Viscosimetric Determination of Transition Points.

By means of an apparatus combining the functions of a viscometer and a stirrer the transition points $Na_2SO_4,10 \rightleftharpoons 0H_2O$, $NiSO_4,7 \rightleftharpoons 6H_2O$, and $Na_2HPO_4,12 \rightleftharpoons 7H_2O$ have been determined.

(III) The System Ferric Oxide-Arsenic Acid-Water at Low Concentrations of Arsenic Acid.

The following solid phases have been found to exist between 2·6 and 23·13% of As_2O_5 in the liquid phase at 25°: Fe_2O_3,As_2O_5,xH_2O (where x is probably near 6); $Fe_2O_3,2As_2O_5,8H_2O$. The latter compound has not been described before, as far as is known. Its existence provides evidence that the ferric arsenates, like the phosphates, are complex. No basic salts were obtained. The system was characterised by an extreme sluggishness in approaching equilibrium.

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(I) THE SYSTEM FERROUS OXIDE-PHOSPHORIC ACID-WATER AND SOME OF ITS OXIDATION PRODUCTS.

(II) AN APPARATUS FOR THE VISCOSIMETRIC DETERMINATION OF TRANSITION POINTS.

(III) THE SYSTEM FERRIC OXIDE-ARSENIC ACID-WATER AT LOW CONCENTRATIONS OF ARSENIC ACID.

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OCTOBER 1927.

INTRODUCTION.

The three subjects forming this thesis are presented hereafter in the form of reprints from the Journal of the Chemical Society, numbered I, II, and III respectively. They are preceded by a reprint of a paper entitled "The System Ferric Oxide-Phosphoric Acid-Water. A New Phosphate.", which embodies the result of work done for the degree of Master of Science in the University of Birmingham. It is included because of its connexion with III, in which frequent reference to it is made, and to a lesser extent with I.

Part of I is not to be considered as belonging to this thesis, namely that dealing with the preparation and analysis of the "amorphous" form of $2FeO,P_2O_5,3H_2O$ (p.367), since it describes work done at the University of Birmingham on the suggestion, and with the advice of Mr S.R. Carter. It has never been presented as part of a thesis for any degree. The remainder of I was done at Bedford College under the author's recognised supervisor for this degree course, Dr J.F. Spencer.

The thesis describes three different investigations which are however closely connected in certain ways. Thus the study of the oxidation products of the ferrous phosphates (I) was the means of throwing fresh light on the composition of the neutral ferric phosphates. The many points of interest shown by the ferric phosphates, particularly those in equilibrium with dilute acid, suggested a search for similar features in the ferric arsenates (III). This last investigation was also carried out in order to test the usefulness of the viscometer-stirrer already used for binary systems (II), in the investigation of ternary systems.

For a summary of the results the abstract accompanying this thesis should be consulted.

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THE SYSTEM FERRIC OXIDE–PHOSPHORIC ACID–WATER. A NEW PHOSPHATE.

BY

SYDNEY RAYMOND CARTER

AND

NORMAN HOLT HARTSHORNE.

From the Transactions of the Chemical Society, 1923. Vol. 123.

CCXLVIII.—*The System Ferric Oxide–Phosphoric Acid–Water. A New Phosphate.*

By SYDNEY RAYMOND CARTER and NORMAN HOLT HARTSHORNE.

THIS work was originally undertaken to throw some light on the interaction between sulphur dioxide and ferrous phosphate. In strong solutions of phosphoric acid, ferrous phosphate is oxidised to a considerable extent by sulphur dioxide, but, on the other hand, sulphur dioxide is unable to reduce ferric phosphate (Wardlaw, Carter, and Clews, T., 1920, **117**, 1241). Further, the oxidation potential of ferrous–ferric mixtures is appreciably lowered by the presence of phosphoric acid (Carter and Clews, unpublished work).

It was thought that a probable explanation of this was to be found in the relative stabilities of the compounds which phosphoric acid forms in solution with ferric phosphate and with ferrous phosphate, respectively, and therefore it was proposed to study both the system with which the paper deals and also its ferrous analogue.

The ferric system has, however, shown so many points of interest and, further, has offered so many experimental difficulties that up to the present we have been unable to complete the second part of our programme and therefore we publish the present work more as an addition to chemical knowledge of the ferric phosphates than as having a bearing on the above problem. We hope to communicate the results of the corresponding ferrous system at a later date.

Cameron and Bell (*J. Physical Chem.*, 1907, **11**, 363) investigated the system between the concentrations 0·942 and 4·706 per cent. of P_2O_5 at 25°. Their results show a continuous change in the composition of the solid phase and would appear to indicate increasing adsorption of phosphoric acid by a compound

$$Fe_2O_3,P_2O_5,xH_2O.$$

Erlenmeyer (*Annalen*, 1878, **194**, 187) prepared three well-defined ferric phosphates to which he assigned the formulæ $Fe_2O_3,P_2O_5,4H_2O$, $Fe_2O_3,2P_2O_5,8H_2O$, and $Fe_2O_3,3P_2O_5,6H_2O$.

He also obtained a series of amorphous products in which the ratio $Fe_2O_3 : P_2O_5$ varied from 8 : 9 to 8 : 11. To these he assigned definite formulæ, but the present work and that of Cameron and Bell led us to the conclusion that they merely represent stages in the adsorption process mentioned above.

Weinland and Ensgraber (*Z. anorg. Chem.*, 1913, **84**, 349) prepared a neutral phosphate by heating ferric chloride with phosphoric acid or with primary potassium phosphate on the water-bath.

This is evidently the same compound as that obtained by Erlenmeyer, who prepared it by boiling either of the acid compounds with water or by heating ferric oxide or hydroxide with phosphoric acid on the water-bath. These workers, however, attribute 5 and not 4 molecules of water to the salt. It is a pink, microcrystalline powder and is not easily dissolved by dilute acids.

Further, they observed a marked difference between this and the product obtained by precipitating ferric salt solutions with alkali phosphates in the cold. This is a yellowish-green, amorphous powder, variable in composition, always containing more acid radicle than is required for a neutral compound, and usually associated with some alkali. It is easily soluble in dilute acids.

Evidence is also produced to show that the so-called acid phosphates are in reality ferriphosphoric acids and that the crystalline neutral phosphate is a ferric salt of one of these. The formulæ they propose are :

$Fe[Fe(PO_4)_2],5H_2O$ for Erlenmeyer's $Fe_2O_3,P_2O_5,4H_2O$.
$H_3[Fe(PO_4)_2],2{\cdot}5H_2O$,, ,, $Fe_2O_3,2P_2O_5,8H_2O$.
$H_6[Fe(PO_4)_3]$,, ,, $Fe_2O_3,3P_2O_5,6H_2O$.

They suggest that the precipitated phosphates are phosphates of aquo-ferric bases.

The System at 25°.

Preliminary experiments were made at this temperature by stirring excess of commercial " pure " ferric phosphate with different strengths of phosphoric acid. The mixtures were made up by grinding the components together in a mortar, filtering the resulting cream through glass wool to remove lumps, and then transferring the filtrates to solubility tubes, in which they were stirred first for one hour at 100° to hasten any chemical change necessary for the attainment of equilibrium and then from three to seven days at 25°. The stirrers were fitted with ground glass bearings in place of the usual mercury seal, and in practice they proved sufficiently air-tight.

When it was thought that equilibrium had been reached, stirring was stopped and the solid phase allowed to settle. By means of an inverted asbestos filter, the liquid phase was drawn off into a weighing bottle and a portion of the moist solid remaining was transferred as quickly as possible to another weighing bottle. The two samples were analysed and the composition of the dry solid determined graphically by the well-known method of Schreinemakers (*Z. physikal. Chem.*, 1893, **11**, 76). Microscopic examinations were also made. The analysis was carried out by dissolving the sample in hydrochloric acid and estimating the iron by titration with potassium dichromate after reduction with stannous chloride.

The phosphate was estimated by titration with uranium acetate after removing the iron by ammonium sulphide. The method of carrying out this latter separation was as follows. The ammonium sulphide was freshly prepared by saturating 5*N*-ammonia with hydrogen sulphide. This was then added in slight excess to the solution to be analysed, and after a few moments' stirring with a rubber-tipped glass rod the whole of the ferrous sulphide aggregated as small flocks. This was filtered off and washed with *N*—2*N*-ammonium sulphide. The whole operation was conducted in the cold. The filtrate was boiled to expel excess of hydrogen sulphide and ammonia. This process usually caused the precipitation of sulphur, but as this passed off with the steam or aggregated to small lumps it did not interfere with the succeeding operations of the analysis. The resulting solution, which thus contained ammonium phosphate and chloride, was then titrated as above.

The results obtained proved to be of little value as an indication of the course of the solubility curve, since it was found later that the ferric phosphate used was contaminated with alkali phosphate and had evidently been prepared by precipitation with this reagent: indeed it appears that the only ferric phosphate obtainable is prepared in this way and therefore is untrustworthy for such work as the present (*vide* Weinland and Ensgraber, *loc. cit.*). The results of Cameron and Bell (*loc. cit.*) may be open to the same criticism, since they state that they used a ferric phosphate which they did not analyse.

At the lowest acid concentrations, however, it has been considered quite permissible to accept the information obtained in regard to the solid phases, since the nature of these would be unaffected by the presence of a soluble impurity such as sodium phosphate. This portion of the work therefore has been combined with that of Cameron and Bell, and the two sets of results are given in Table I below and are plotted in Fig. 1.

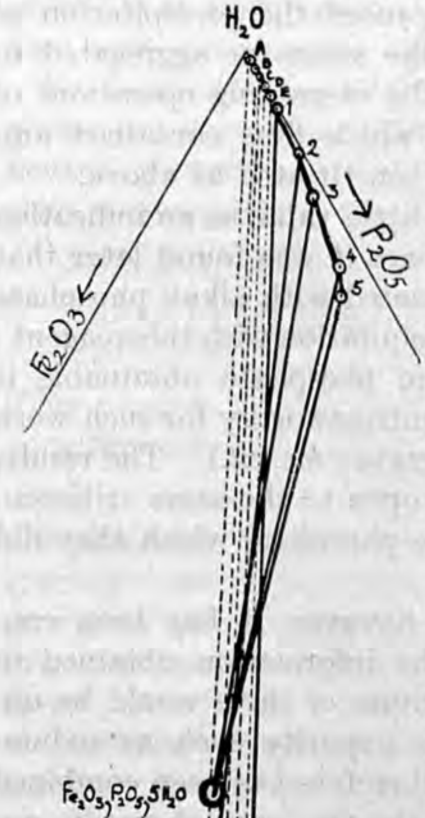
TABLE I.

Ferric phosphate mixtures at 25°.

	Liquid phase.		Moist solid phase.		
Mixture.	% Fe_2O_3.	% P_2O_5.	% Fe_2O_3.	% P_2O_5.	
A	0·0105	0·942	15·11	13·81	Cameron and Bell
B	0·0205	1·984	19·35	17·90	
C	0·0384	2·838	23·11	22·54	
D	0·0611	3·770	15·13	17·73	
E	0·0849	4·706	20·43	23·37	
1	Trace	5·93	9·57	14·3	
2	0·23	10·1	11·35	17·5	
3	1·40	14·1	24·40	27·1	
4	2·43	19·8	21·49	27·7	
5	4·42	21·7	21·36	28·3	
*					

It will be seen that, as previously stated, Cameron and Bell's results (broken lines in Fig. 1) show a continuous change in the composition of the solid phase and would appear to indicate adsorption of acid by a compound of the formula Fe_2O_3,P_2O_5,xH_2O, since the left-hand conjugation line (A) almost coincides with the imaginary line drawn from the H_2O corner through the point $Fe_2O_3,P_2O_5,5H_2O$. In the present work, mixture 1 gives a line in conformity with this. Mixture 2, however, shows a complete change, the line passing very close to the compound $Fe_2O_3,P_2O_5,5H_2O$, and mixtures 3, 4, and 5 produce lines actually converging on this point.

FIG. 1.



Thus it appears that at the lowest acid concentrations there exists a neutral compound which adsorbs more or less acid, according to the concentration in the liquid phase, and that the phosphates of variable composition described by Weinland and Ensgraber (*loc. cit.*) and also the precipitates of Erlenmeyer (*loc. cit.*) are merely different stages in this adsorption process.

At higher acid concentrations, we have a definite compound which is clearly the $Fe_2O_3,P_2O_5,4(\text{or } 5)H_2O$ described by the above workers. It will be seen that the present results support the contention of Weinland and Ensgraber that there are 5 and not 4 molecules of water as proposed by Erlenmeyer. In this connexion, it is interesting to note that the latter's figures would have fitted equally well a compound having $4{\cdot}5H_2O$. His theory certainly finds support in the composition of the mineral strengite, $FePO_4,2H_2O$, but this was probably formed under very different conditions.

The difference in behaviour evinced by the two forms of neutral phosphate is evidently to be explained by a fundamental difference in constitution. It will have been seen in the early part of this paper that Weinland and Ensgraber have already indicated as much, and in the light of the present results we may advance the still more definite view that the one compound is a true ferric phosphate capable of adsorbing phosphoric acid, whilst the other is a ferric ferriphosphate, $Fe[Fe(PO_4)_2],5H_2O$.

Microscopic examination of the two forms failed to reveal any great difference. Both appeared to be amorphous, although $Fe_2O_3,P_2O_5,5H_2O$ was certainly the more granular. It did not, however, exhibit a definite crystalline form as described by Weinland and Ensgraber. Probably this was on account of its method of preparation; Erlenmeyer too describes it as a granular powder.

Returning now to the determination of the solubility curve and the solid phases stable at the higher acid concentrations, it has been seen that the use of commercial ferric phosphate is not to be recommended. During an examination of the possibilities of new starting points, a phosphate was prepared from an oxidised solution of pure iron wire in concentrated phosphoric acid by precipitation with a large volume of water. The product, which was a pinkish-white, amorphous powder, gave the following results on analysis: $Fe_2O_3 = 32{\cdot}0$; $P_2O_5 = 34{\cdot}8$; $H_2O = 33{\cdot}1$ per cent., in which the molecular ratio $Fe_2O_3 : P_2O_5 = 1 : 1{\cdot}23$.

On being stirred with phosphoric acid, however, it was found to set up metastable equilibria not easily disturbed and therefore its use was abandoned.

Attention was next directed to the possibilities of ferric hydroxide. Since at 25° this dissolves in phosphoric acid with extreme reluctance, about one month's very rapid stirring being found necessary, experiments were made in which it was stirred first at 100° until all the red colour had disappeared and then at 25°. The results, however, at the higher acid concentrations, particularly where the liquid was more viscous, proved to be most irregular and led us to conclude that a true equilibrium was not being attained. It appears that the only sure way of avoiding the formation of metastable phases is to stir the mixtures solely at the temperature of the isotherm required and this consideration led us to abandon the work at 25° and select a higher temperature. 70° was chosen, since this is the lowest temperature, expressed in round numbers, at which ferric hydroxide dissolves in phosphoric acid in the space of a few hours.

The System at 70°.

Experimental difficulties in the collection of samples of liquid and moist solid phases increase at the higher temperatures, particularly when, as in the present case, many of the mixtures, are extremely viscous, difficult to filter, and possess solid phases which are hygroscopic. To combat these difficulties, special apparatus was devised the description of which is given in the next section.

The general experimental procedure for the study of the 70°

isotherm was as follows. The mixtures were prepared by grinding together the necessary quantities of ferric hydroxide, phosphoric acid, and water in a glass mortar and then stirring in a solubility bottle in a thermostat. The latter was fitted with a glass window to enable the contents of the bottle to be observed without having to withdraw it from the bath. It was well lagged with asbestos and a small Bunsen flame (controlled by the ordinary type of regulator) was found to be sufficient to keep it at 70°. Undue evaporation was prevented by covering the surface of the water with a layer of paraffin wax.

The attainment of equilibrium was determined by withdrawing samples of the liquid phase from day to day and estimating the iron by titration with potassium dichromate solution until constant values were obtained. In most cases it was found that four to five days were required, but the mixtures were usually stirred for considerably longer periods than this.

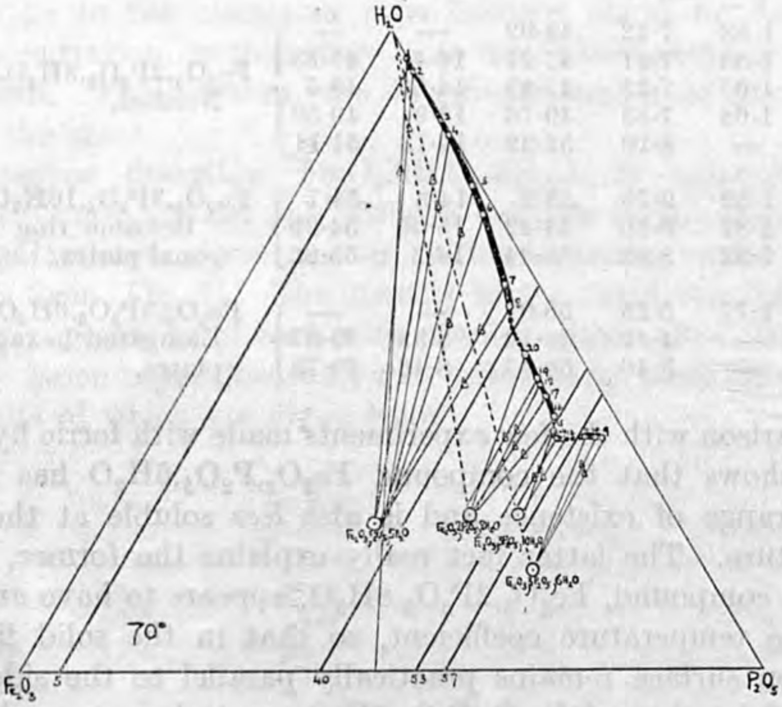
The ferric hydroxide used was prepared by precipitating with ammonia a nearly boiling solution of 40—50 grams of ferric chloride in 2 litres of water. The mixture was meanwhile stirred mechanically and after about half an hour was allowed to settle. The hydroxide was then washed by decantation, being reheated and stirred after every fresh addition of water, until it showed signs of becoming colloidal, after which it was filtered and washed until it gave only a very faint chloride reaction. It was not found possible to wash it quite free from electrolyte. It was then either dried at 100° and finely powdered or, in the case of mixtures weak in acid, used without further treatment. The acid, which was the same as that used at 25°, was a perfectly clear and colourless liquid described as Syrupy Phosphoric Acid, sp. gr. 1·75. It was found to be free from meta- and pyro-phosphates, phosphites, nitrates, metals, and silica, but contained traces of sulphates, chlorides, and arsenic.

On equilibrium being attained, samples of both liquid and moist solid phases were withdrawn and analysed for Fe_2O_3 and P_2O_5 by the methods used at 25°, with the exception that in the latter case the magnesium pyrophosphate determination (Schmitz's method, Treadwell and Hall's "Analytical Chemistry," Vol. II, p. 434) was substituted for the uranium acetate titration as being more accurate. The solids were examined microscopically as before. In addition, rough density determinations of most of the liquid phases were made by weighing about 1·5 c.c. in a calibrated pyknometer.

After the removal of the samples from the solubility bottle, water or acid was added, the mixture again stirred, and fresh determinations were made. In this way, it was possible to investigate a considerable portion of the isotherm with one original solution. The breaks in the curve were approached from both sides, and by appropriate seeding it was ensured that the equilibria examined were not metastable. The results obtained are plotted in Fig. 2 and are tabulated below. Photomicrographs of the crystalline solid phases are shown in Figs. 4—7.

Owing to the experimental difficulties, the direction of the conjugation lines has not proved to be as accurate as is desirable. However, by taking into consideration the work at 25° and the composition of the already known compounds, we have been able to arrive at the formulæ given in Table II for the solid phases. The breaks have not been determined experimentally, but their approximate positions are evident from the shape of the curve or the direction of the conjugation lines as the case may be. The lines drawn parallel to the H_2O–Fe_2O_3 side of the triangle in Fig. 2 indicate that they occur near 5, 40, 53, and 57 per cent. of P_2O_5, and these concentrations correspond to 2·1, 26, 41, and 43 *N*-(gram equivalent)-solutions of phosphoric acid, respectively.

FIG. 2.



Dealing now with the solid phases in detail, we see that mixture 1 shows far less associated acid than a corresponding mixture at 25°. This decrease with rise of temperature bears out the contention that the change in solid phase composition in this area is due to adsorption.

TABLE II.

The System at 70°.

Mixture.	$d_{20^\circ}^{20^\circ}$.	Liquid phase.		Moist solid phase.		Composition and microscopic examination of solid phase.
		Fe_2O_3 %.	P_2O_5 %.	Fe_2O_3 %.	P_2O_5 %.	
1	—	trace	4·07	9·9	12·26	Fe_2O_3,P_2O_5,xH_2O and adsorbed acid. Amorphous.
2	—	under 0·1	6·38	5·1	9·99	$Fe_2O_3,P_2O_5,5H_2O$. No definite crystalline form visible.
3	—	0·195	14·08	6·00	17·24	
4	—	0·252	16·24	7·35	20·00	
5	—	1·08	23·56	6·29	25·45	
6	—	1·85	27·03	15·25	30·81	
7	—	4·49	35·46	11·4	35·75	
8	1·45	5·45	37·43	17·8	37·33	
20	1·58	7·12	43·92	—	—	$Fe_2O_3,2P_2O_5,8H_2O$. Needles.
19	1·63	7·21	47·27	16·4	47·33	
18	1·65	7·25	47·87	14·66	48·5	
17	1·68	7·53	49·76	15·9	49·50	
16	—	8·10	52·32	15·13	51·11	
15	1·82	9·79	53·2	14·3	54·7	$Fe_2O_3,3P_2O_5,10H_2O$. "Benzene ring" hexagonal plates.
14	1·82	9·50	54·42	15·00	54·29	
13	1·82	8·68	55·84	14·2	55·86	
11	1·77	5·28	58·07	—	—	$Fe_2O_3,3P_2O_5,6H_2O$. Elongated hexagonal plates.
10	—	4·42	59·12	8·38	59·57	
9	—	3·46	60·47	8·46	60·73	

Comparison with the few experiments made with ferric hydroxide at 25° shows that the compound $Fe_2O_3,P_2O_5,5H_2O$ has a much greater range of existence and is also *less* soluble at the higher temperature. The latter fact really explains the former, because the next compound, $Fe_2O_3,2P_2O_5,8H_2O$, appears to have an almost negligible temperature coefficient, so that in the solid figure its saturation surface remains practically parallel to the side of the prism, whilst that of $Fe_2O_3,P_2O_5,5H_2O$ must slope towards it and so spread over its neighbour with rise of temperature.

As at 25°, both the neutral phosphates failed to reveal any definite crystalline form when examined under the microscope.

The diacid compound, $Fe_2O_3,2P_2O_5,8H_2O$, which has just been mentioned requires little further comment except that whereas Erlenmeyer described it as crystallising in four-sided prisms, our product invariably appeared as needles with pointed ends (Fig. 4), which, of course, may have been merely a distorted form.

The most interesting feature of the results is that they reveal the existence of a compound which, so far as is known, has not been described before, and to which we have assigned the formula $Fe_2O_3,3P_2O_5,10H_2O$. This composition is only tentatively advanced at present, since it is based solely on the three conjugation lines

13, 14, and 15, which are not very definite as regards their destination. It is, however, the only formula which can be reconciled with them, having regard to what is to be expected in this region of the isotherm, namely, a higher hydrate of $Fe_2O_3,3P_2O_5,6H_2O$. If we accept Weinland and Ensgraber's co-ordination formula for the latter, the new compound merely becomes its dihydrate, $[Fe(PO)_3]H_6,2H_2O$.

It crystallises in hexagonal plates, perfect specimens bearing a striking resemblance to the conventional benzene ring (Fig. 5). It was at first thought that they were another form of the elongated hexagonal plates of $Fe_2O_3,3P_2O_5,6H_2O$ (Fig. 6), but in addition to the evidence furnished by the conjugation lines we have actually followed under the microscope the transition from the "benzene ring" type to the elongated type brought about by raising the acid concentration, so that there is no doubt that they are different compounds. Furthermore, the interfacial angles of the crystals are not the same.

Erlenmeyer describes $Fe_2O_3,3P_2O_5,6H_2O$ as crystallising in rhombic plates, and on subjecting a suitable liquid phase to the isothermal removal of water at 70° (without stirring) we too obtained it in this form (Fig. 7). The identity of the two forms was proved by drying specimens of each with absolute ether after the manner used by Erlenmeyer (*loc. cit.*) and submitting them to analysis, the results of which are given below.

	Rhombic plates. Found.	Elongated hexagonal plates. Found.	Required for $Fe_2O_3,3P_2O_5,6H_2O$.	Required for $Fe_2O_3,3P_2O_5,10H_2O$.
Fe_2O_3	22·9	23·0	23·0	20·9
P_2O_5	60·0	59·0	61·4	55·7
H_2O (by difference)	17·1	18·0	15·6	23·5

We have not been able to apply such a confirmatory test to the constitution of the new compound, since up to the present we have been unsuccessful in obtaining a sufficient quantity to manipulate in the drying apparatus.

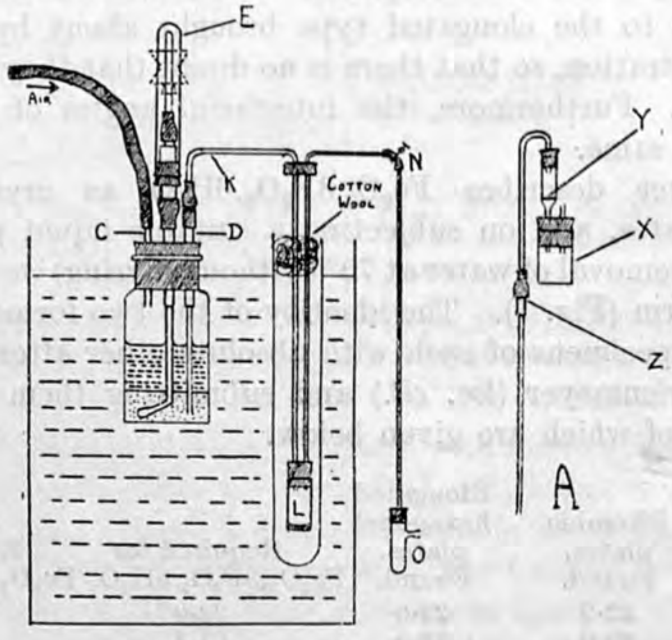
All the solid phases were pinkish-white, whilst the colour of the liquid phase varied from colourless to deep rose-pink with increasing acid concentration up to mixture 13, after which it became decidedly brown. This latter colour therefore appears to be a property of $Fe_2O_3,3P_2O_5,6H_2O$ when in solution, although in the solid state it is pinkish-white, as already stated.

From the dotted lines joining the H_2O corner of the triangle with the points representing the three acid compounds, it will be seen that each of these is decomposed by water with formation of the neutral compound which in the case of two of them is in conformity with Erlenmeyer's work.

Method of Collecting Phase Samples at 70°.

The apparatus is shown in Fig. 3. To collect a sample of moist solid the pulley on the axis of the stirrer (shown dotted) was replaced by the air-tight tube *E*, and after the solid had subsided dry compressed air was admitted at *C* so as to force the sludge into the weighed collector, *L*, the base of which was formed of a perforated filter-plate covered with asbestos. In this operation, the tube *O* acted as an overflow trap, whilst the clip, *N*, regulated the admission of the sludge to *L*. By raising the tube *K* and closing *N* the compressed air was made to express liquid from the sample in *L*, which was then removed, closed with ground stoppers, and weighed. The sample was subsequently dissolved out and examined. The filtration was thus carried out at the temperature of the thermostat, a precaution which was necessary on account of the length of time required by some of the more viscous mixtures.

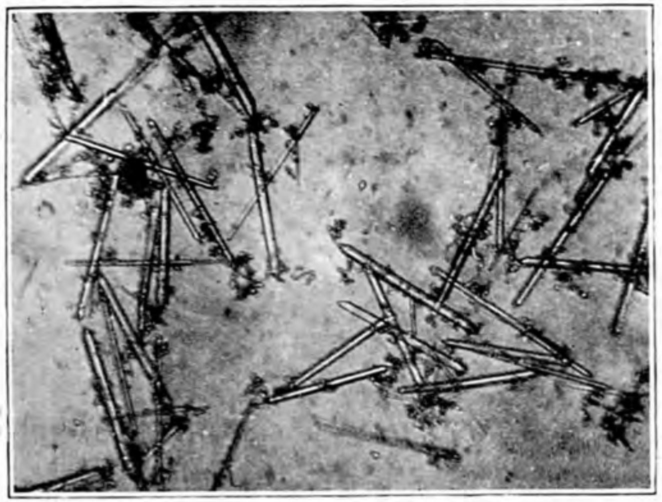
FIG. 3.



For the collection of liquid samples a separate apparatus, *A*, was employed, since this operation was of frequent occurrence and something more simple to manipulate was desirable. It was connected to the solubility bottle through the tube *D* in place of the moist solid collector by means of the sliding connexion, *Z*, and, after suitable adjustment, the specimen was blown over into the weighing bottle, *X*, through the filter, *Y*.

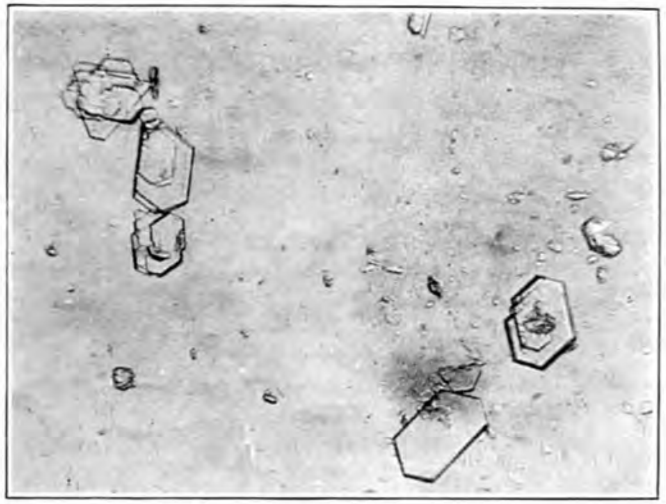
It is probable that these methods will prove useful in other

FIG. 4.



$Fe_2O_3,2P_2O_5,8H_2O$. Magnification × 75.

FIG. 5.

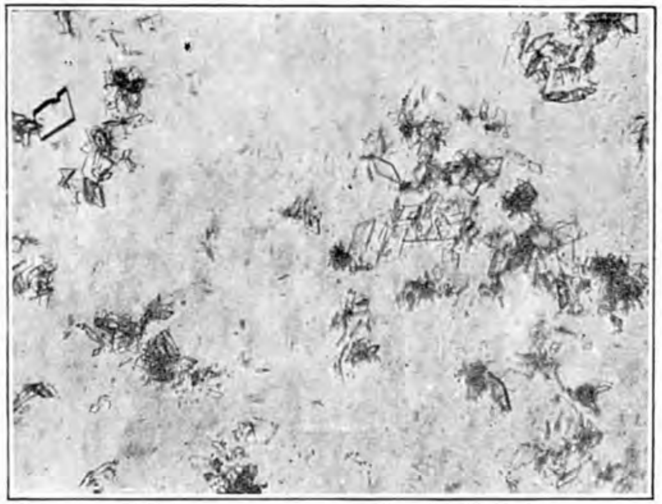


$Fe_2O_3,3P_2O_5,10H_2O$. × 75.

FIG. 6.

$Fe_2O_3,3P_2O_5,6H_2O$. Elongated hexagonal plates × 75.

FIG. 7.



$Fe_2O_3,3P_2O_5,6H_2O$. Rhombic plates × 75.

[*To face Trans.*, p. 2232.]

equilibria investigations, particularly those involving viscous liquids at high temperatures.

Summary.

The system ferric oxide–phosphoric acid–water has been studied at 25° and 70°.

At 25°, we have been able to co-ordinate the work of previous investigators on the neutral ferric phosphates. It appears that at the lowest acid concentrations a compound, Fe_2O_3,P_2O_5,xH_2O, is stable which adsorbs phosphoric acid from the mother-liquor, and is probably a true ferric phosphate. At higher concentrations, this changes to a compound, $Fe_2O_3,P_2O_5,5H_2O$, which has no adsorptive power and is probably a ferric ferriphosphate.

At 70°, we have shown the existence of the above solid phases, the compounds $Fe_2O_3,2P_2O_5,8H_2O$ and $Fe_2O_3,3P_2O_5,6H_2O$ which are already known, and also that of a new compound to which we have assigned the formula $Fe_2O_3,3P_2O_5,10H_2O$.

In conclusion, one of us (N. H. H.) desires to thank the Department of Scientific and Industrial Research for a grant which enabled a portion of this work to be carried out.

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EDGBASTON, BIRMINGHAM.

[*Received, May 29th*, 1923.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

I

THE SYSTEM FERROUS OXIDE–PHOSPHORIC ACID–WATER AND SOME OF ITS OXIDATION PRODUCTS.

BY

SYDNEY RAYMOND CARTER

AND

NORMAN HOLT HARTSHORNE.

Reprinted from the Journal of the Chemical Society,
February, 1926.

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

By SYDNEY RAYMOND CARTER and NORMAN HOLT HARTSHORNE.

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.

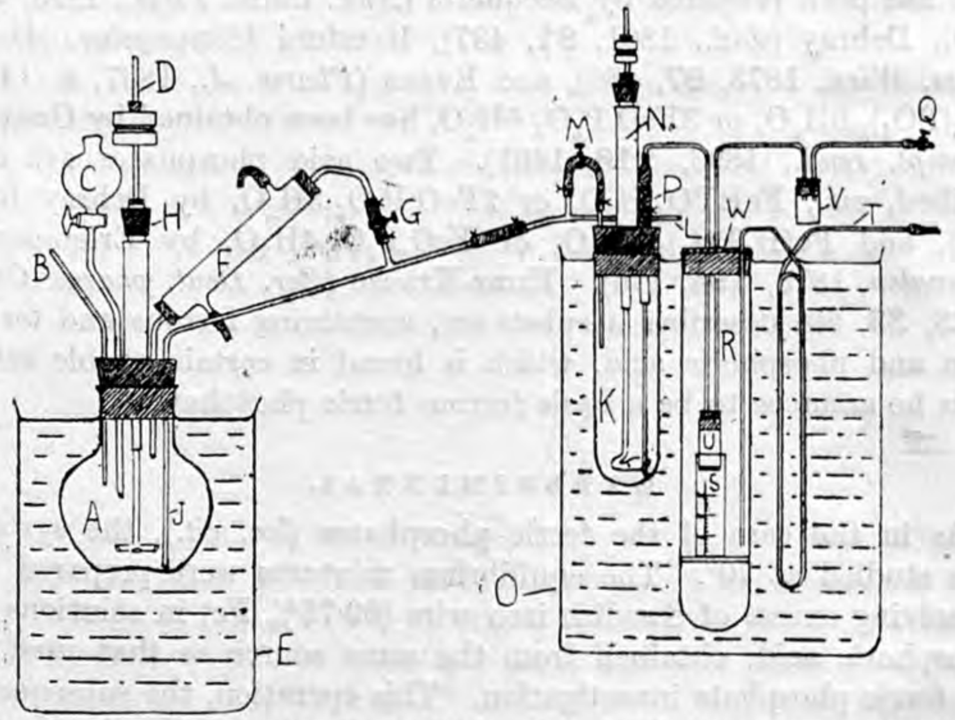
The following ferrous phosphates are described in the literature: $Fe_3(PO_4)_2,8H_2O$, or $3FeO,P_2O_5,8H_2O$, occurs in nature as *vivianite* and has been prepared by Becquerel (*Ann. Chim. Phys.*, 1833, **54**, 149), Debray (*ibid.*, 1861, **61**, 437), Horsford (*Sitzungsber. Akad. Wiss. Wien*, 1873, **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.

		Liquid phase.			Moist solid phase.		
Mixture.	% oxidation.	$d_{4°}^{15-20°}$.	% FeO.	% P_2O_5.	% FeO.	% P_2O_5.	Solid phase.
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.

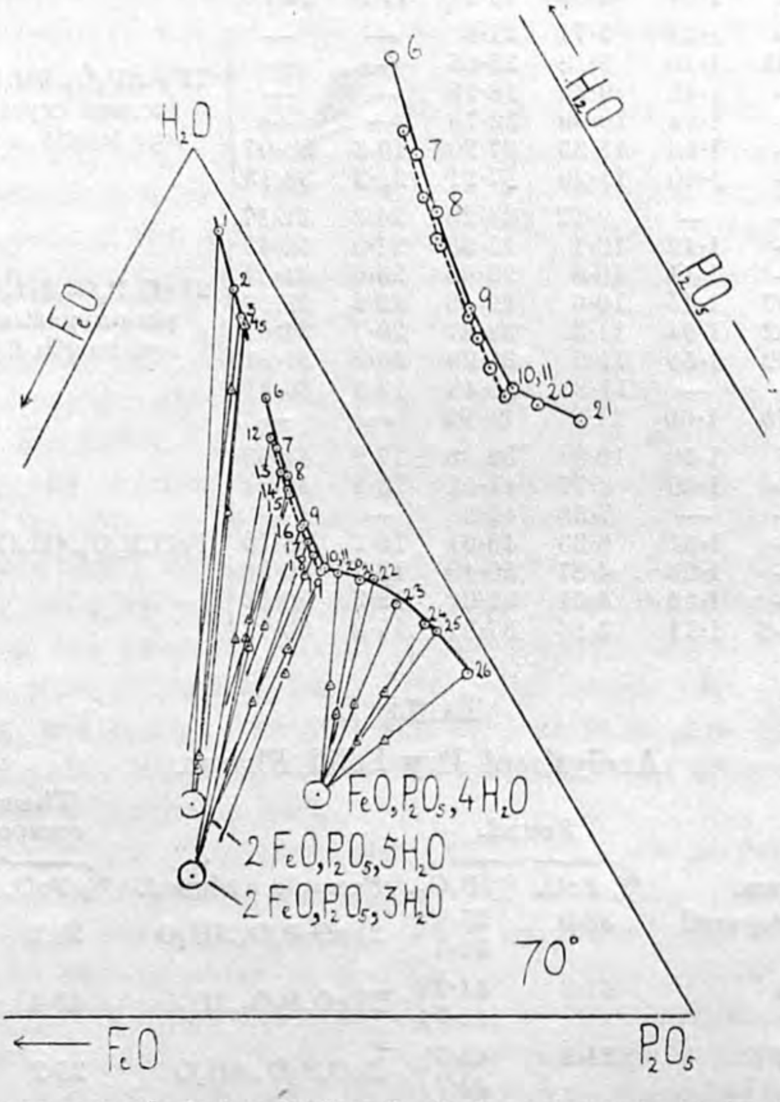
Analysis of Dry Solid Phases.

	Found.			Theoretical composition.	
Mixture.	% FeO.	% P_2O_5.	Formula assigned.	% 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

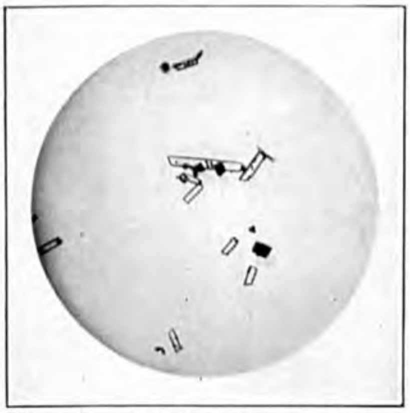


FIG. 3.—$2FeO,P_2O_5,5H_2O$ and β-$Fe_2O_3,P_2O_5,4H_2O$ (short dark prisms). ×10.

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

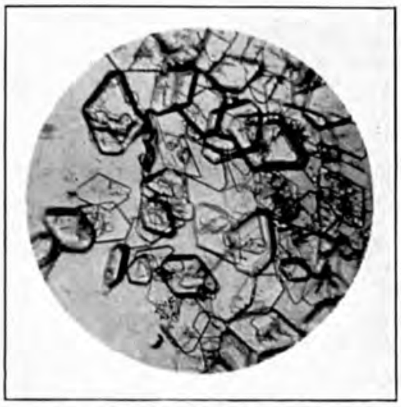


FIG. 5.—$2FeO,P_2O_5.3H_2O$ (crystalline). × 57.

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.

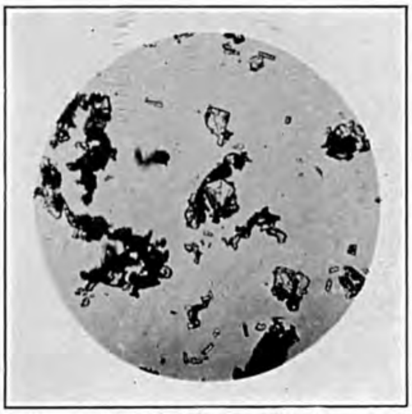


FIG. 9.—α-$Fe_2O_3,P_2O_5,4H_2O$. × 90

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.

The authors wish to express their indebtedness to Dr. J. F. Spencer for much helpful advice and to Mr. A. Watson for carrying out many of the analyses.

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[*Received, December* 16*th*, 1925.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

II

AN APPARATUS FOR THE VISCOSIMETRIC DETERMINATION OF TRANSITION POINTS.

BY

NORMAN HOLT HARTSHORNE

From the Transactions of the Chemical Society, 1924. Vol. 125.

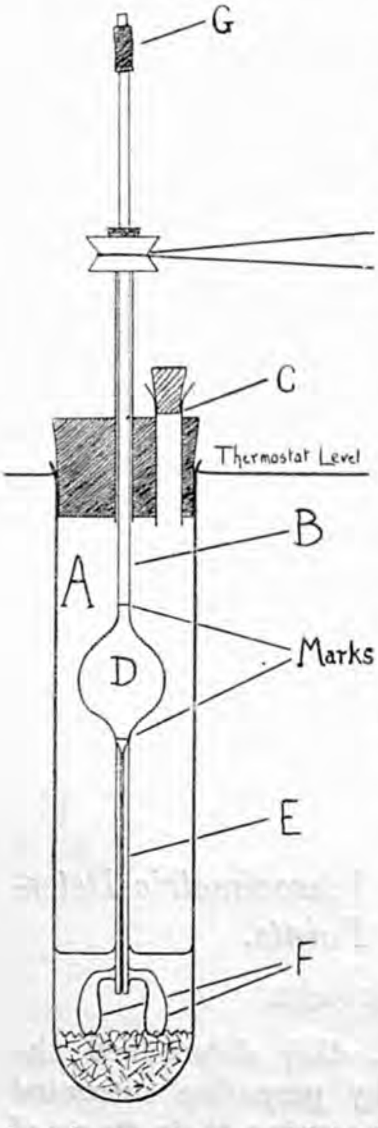
CCLXXIV.—*An Apparatus for the Viscosimetric Determination of Transition Points.*

By Norman Holt Hartshorne.

Dunstan and Langton (J., 1912, **101**, 418) determined the transition points of a number of salts by preparing saturated solutions at different temperatures and measuring their times of flow in a viscosimeter of the Ostwald type. In the apparatus now described, successive solutions are prepared and their times of flow determined in one and the same vessel, thereby effecting a considerable saving of time.

The apparatus (Fig. 1) consists of a solubility tube, *A*, 25 cm. long and 5 to 6 cm. wide, fitted with a rubber bung carrying a combined viscosimeter and stirrer, *B*, and a wide tube, *C*, which normally is closed with a cork. The bulb, *D*, of the viscosimeter has a capacity of about 20 c.c. The capillary, *E*, is 10 cm. long, and its bore is varied to suit the nature of the substance to be examined; in the present work, about 0·75 mm. was found to be suitable, and this would probably be so for all salts of average solubility. Glass paddles, *F*, are sealed on the capillary about 0·5 cm. from the end.

FIG. 1.



To carry out a determination, about 80 c.c. of the saturated solution together with excess salt are placed in *A* and the apparatus is fitted together and immersed in a glass-sided thermostat (regulated to ± 0·02°). The viscosimeter, closed by a rubber cap, *G*, to exclude dust, is rotated until equilibrium is reached, the solid is allowed to settle completely, and *G* is replaced by a piece of rubber tubing by means of which solution is sucked up beyond the higher mark. The viscosimeter is raised clear of the remaining liquid, and its contents are allowed to drop back, the time of flow from the upper to the lower mark being noted. After a duplicate reading has been made in the same way, the viscosimeter is washed down with distilled water (2 c.c.), *G* is replaced, and the solution stirred again at another temperature. By means of additions or withdrawals through the tube *C*, the quantities of solid and solution can be adjusted when necessary. The time taken to reach equilibrium can readily be determined by taking readings at the same temperature until the results are constant. In the present work, 6 hours were usually found to be sufficient, but in most cases 12 to 24 hours were allowed.

The following transition points have been determined :—

$$Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4+10H_2O.$$
$$NiSO_4,7H_2O \rightleftharpoons NiSO_4,6H_2O(\text{blue})+H_2O.$$
$$Na_2HPO_4,12H_2O \rightleftharpoons Na_2HPO_4,7H_2O + 5H_2O.$$

The results are given below, the time of flow being recorded in seconds.

Sodium Sulphate.

$Na_2SO_4,10H_2O$. 20·0°, 133; 22·7°, 140; 23·0°, 142; 24·2°, 144; 26·5°, 156; 26·7°, 157; 29·6°, 174; 30·5°, 184; 32·5°, 219; 32·6°, 221; 32·7°, 225.

Na_2SO_4. 25·1°, 289; 26·1°, 277; 31·0°, 232; 32·0°, 225; 32·8°, 219; 33·2°, 215; 33·8°, 214; 34·8°, 205; 35·0°, 205; 35·9°, 198; 36·8°, 192; 38·4°, 183.

Nickel Sulphate.

$NiSO_4,7H_2O$. 21·4°, 355; 24·5°, 350; 27·0°, 347; 27·7°, 347; 28·1°, 347; 31·4°, 347; 34·3°, 347.

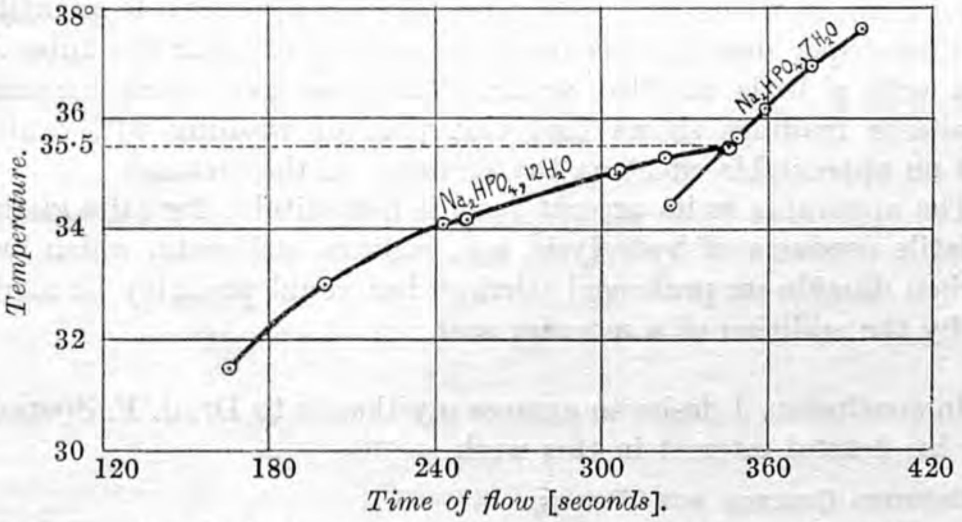
$NiSO_4,6H_2O$ (blue). 25·1°, 367; 25·8°, 361; 27·0°, 356; 29·1°, 349; 29·8°, 345; 30·1°, 343; 30·6°, 342; 32·1°, 336; 33·7°, 331; 34·5°, 329.

Disodium hydrogen phosphate.

$Na_2HPO_4,12H_2O$. 31·5°, 166; 33·0°, 200; 34·1°, 243; 34·2°, 252; 35·0°, 305; 35·05°, 306; 35·3°, 323; 35·5°, 346.

$Na_2HPO_4,7H_2O$. 34·45°, 325; 35·65°, 349; 36·2°, 359; 36·95°, 377; 37·65°, 395.

FIG. 2.



In the experiments with sodium sulphate and nickel sulphate the temperature regulation was not so sensitive as is desirable and the results when plotted show small irregularities. The transition points deduced from them are 32·55° for sodium sulphate (Richards and Wells, *Z. physikal. Chem.*, 1903, **43**, 471, found 32·383° on the hydrogen scale, whilst Berkeley, *Phil. Trans.*, 1904, **203**, [*A*], 209, and Gay-Lussac, *Ann. chim. phys.*, 1819, **11**, 312, found 32·5°) and 29·3° for nickel sulphate (Steele and Johnson, J., 1904, **85**, 113, found 31·5°). The low result in the case of nickel sulphate is attributed to impurity.

In the case of disodium hydrogen phosphate, the temperature was regulated to within ± 0·02° and the curve (Fig. 2) is markedly more regular. The transition point obtained is 35·5°. Values given by previous workers are 36·4° (Person, *Ann. chim. phys.*, 1849, [iii], **27**, 253), 35·0° (Tilden, J., 1884, **45**, 268), *ca.* 36·6° (Baur, *Z. physikal. Chem.*, 1895, **18**, 180), and 35·4° (D'Ans and Schreiner, *ibid.*, 1911, **75**, 99). The value obtained is thus in good agreement with the latest work. The salt used was B.D.H. ordinary reagent and was twice recrystallised, the crystals being washed with ice-water.

The reproducibility of the curves was shown by repeating portions of them; the figures so obtained are included in those given above. Duplicate readings were taken at all temperatures and never varied by more than 1 second, the agreement being usually within 0·5 second. Failure to reach this points to an obstruction in the capillary tube, which sometimes occurs when the viscosimeter has not been washed. A less frequent cause is the presence of dust in the solution, which should therefore be filtered before being poured into the apparatus. For a similar reason, it is better not to dry the solids with filter-paper after recrystallisation. In all cases except one, in which the solution contained a considerable quantity of filter-paper dust, it was found quite easy to clear the tube *in situ* with a little distilled water. The close agreement between duplicate readings shows that this plan of washing with water has no appreciable effect on the accuracy of the method.

The apparatus in its present form is not suitable for salts giving volatile products of hydrolysis, *e.g.*, sodium carbonate, which lost carbon dioxide on prolonged stirring, but could probably be made so by the addition of a mercury seal.

In conclusion, I desire to express my thanks to Dr. J. F. Spencer for his helpful interest in this work.

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[*Received, July 25th,* 1924.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

III

THE SYSTEM FERRIC OXIDE–ARSENIC ACID–WATER AT LOW CONCENTRATIONS OF ARSENIC ACID.

BY

NORMAN HOLT HARTSHORNE.

Reprinted from the Journal of the Chemical Society,
August 1927.

Reprinted from the Journal of the Chemical Society, 1927.

CCXXX.—*The System Ferric Oxide–Arsenic Acid–Water at Low Concentrations of Arsenic Acid.*

By NORMAN HOLT HARTSHORNE.

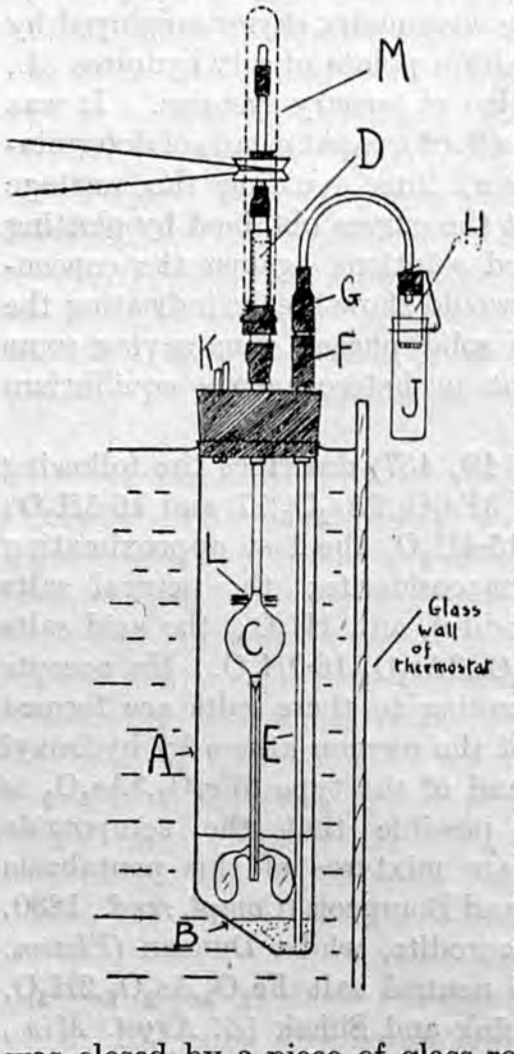
THIS work was undertaken (*a*) to discover whether any of the numerous ferric arsenates described in the literature were merely stages in a series of adsorption compounds, as in the case of the ferric phosphates (Carter and Hartshorne, J., 1923, **123**, 2223); and (*b*) to test the usefulness of the viscometer-stirrer employed by the author to determine the transition points of salt hydrates (J., 1924, **125**, 2097) in the investigation of ternary systems. It was thought that this apparatus would afford a rapid means of determining the attainment of equilibrium, thus avoiding the wastage involved in test analyses, and that the curves obtained by plotting the time of flow of the saturated solutions against the concentration of one of the components would show breaks indicating the limits of stability of the various solid phases, thus saving some of the laborious analyses inherent in heterogeneous equilibrium work.

Metzke (*Z. anorg. Chem.*, 1899, **19**, 457) describes the following ferric arsenates: The basic salts, $3Fe_2O_3,2As_2O_5,17$ and $16{\cdot}5H_2O$; $4Fe_2O_3,3As_2O_5$, 33·5, 20·5, and $15{\cdot}4H_2O$, the last approximating to the naturally occurring pharmacosiderite; the neutral salts $Fe_2O_3,As_2O_5,10,9,4$ (artificial scorodite), and $1H_2O$; the acid salts $2Fe_2O_3,3As_2O_5,22{\cdot}5H_2O$ and $Fe_2O_3,3As_2O_5,16{\cdot}7H_2O$. He accepts the view that the acids corresponding to these salts are formed from As_2O_5 by the replacement of the oxygen atoms by hydroxyl groups. On this basis, a compound of the type $5Fe_2O_3,3As_2O_5$ is missing, but Metzke thinks it possible that the compounds $3Fe_2O_3,2As_2O_5,17$ and $16{\cdot}5H_2O$ are mixtures of this pentabasic salt with one less basic. Verneuil and Bourgeois (*Compt. rend.*, 1880, **90**, 223) also prepared artificial scorodite, whilst Duncan (*Pharm. J.*, 1905, **20**, 223) describes the neutral salt $Fe_2O_3,As_2O_5,2H_2O$, which is dehydrated at 100°. Ježek and Sim̆ek (*Z. Kryst. Min.*, 1914, **54**, 88) state that an anhydrous neutral salt is formed as a deposit of black prismatic crystals in the Deacon chlorine process. Other ferric arsenates, most of which approximate to those given above, are described by workers in the early part of the last century, notably Berzelius, but the inaccurate analytical methods available at that time and the exhaustive nature of Metzke's researches make it unnecessary to specify them. The following ferric arsenates occur in nature: pharmacosiderite, $4Fe_2O_3,3As_2O_5,15H_2O$; white iron-sinter, $2Fe_2O_3,As_2O_5,12H_2O$; and scorodite, $Fe_2O_3,As_2O_5,4H_2O$.

EXPERIMENTAL.

The system was studied at 25°. The apparatus used for preparing the equilibrium mixtures and collecting the phase samples is shown in Fig. 1. The solubility tube, A, was about 6 cm. wide and 26 cm. long, having a bottom so shaped as to collect the solid at the foot of the tube, E. This shape is very useful when (as was often the case in the present investigation) the amount of solid is small. It is important that the sloping portion, B, should be sufficiently steep. The viscometer-stirrer, C, was the same as that used in the previous work (*loc. cit.*), *i.e.*, with a capillary diameter of about 0·75 mm. It was supported by a glass bearing with thrust surfaces ground to a good fit and packed with vaseline contained in the tube, D. This type of bearing is simple to make, trustworthy, and sufficiently air-tight in cases where rigorous sealing of the solubility tube is unnecessary. Any vaseline which ran down the stem of the viscometer was caught by the rings of filter paper at L. These were changed occasionally and were quite effective in preventing contamination of the mixtures. The apparatus for collecting the phase samples is shown connected to the solubility tube by means of the rubber tube, F (which normally was closed by a piece of glass rod), and the sliding connexion, G. It consisted of the collecting tube, E, the weighed filter, H, and the weighing bottle, J, being thus merely a modification of the apparatus used previously for ferric and ferrous phosphates (*loc. cit.*; Carter and Hartshorne, J., 1926, 363), the most important difference being that it was not now necessary to filter the samples at thermostat temperature, since this was not far removed from that of the room. Dry air for forcing the samples through the filter was admitted through the tube, K. During this operation,

FIG. 1.



the stirrer bearing was sealed by the tube, M, after removal of the pulley. The samples were subsequently dissolved in hydrochloric acid and diluted to a standard volume. The solubility tube was supported in a glass-sided thermostat maintained at 25° ± 0·02° by means of an ordinary gas regulator.

Some difficulty was experienced in finding a suitable starting point for the preparation of the equilibrium mixtures. Arsenic acid ($H_3AsO_4,\frac{1}{2}H_2O$) was prepared by the oxidation of A.R. arsenious oxide (B.D.H.) according to the method described in Vanino's "Präparative Chemie," 1921, Vol. I, p. 215. Ferric hydroxide, prepared by the method used in the ferric phosphate work, could not, however, be dissolved in a solution of the arsenic acid; in spite of many variations in the conditions, only very small proportions were attacked. This is no doubt to be attributed to the small solubility of the ferric arsenates in arsenic acid, for in some cases microscopic examination showed that the ferric hydroxide particles were coated with arsenate, which prevented further action. It has been found that in solutions containing up to 22% of As_2O_5 the solubility at 25° never exceeds 0·1% of Fe_2O_3. The difficulty was eventually overcome by adding hydrochloric acid to the mixture. The ferric chloride thus formed reacted with the arsenic acid, and on repeated evaporation to dryness the ferric arsenate was freed from all but a trace of hydrochloric acid. The mixture, especially when concentrated, had a greenish-blue tint. On one occasion after an evaporation disc-shaped particles separated similar to those observed by Metzke (*loc. cit.*) when attempting to prepare artificial scorodite. The greenish-blue colour of these and other preparations is also mentioned by Metzke and is evidently due to a complex ferriarsenic acid or acids, analogous to the pink ferriphosphoric acids. This view is supported by the observations of Metzke and earlier workers, that the neutral and acid arsenates dissolve in concentrated ammonia, and by that of Duncan (*loc. cit.*), that oxidised solutions of ferrous arsenates respond very faintly to the thiocyanate test for ferric iron.

The mixture thus prepared was the basis of all the equilibrium mixtures studied. A portion, suitably diluted with water and freed from large lumps of solid, was transferred to the solubility tube, and after equilibrium had been reached and the necessary phase samples collected, water or syrupy acid was added and a new equilibrium reached, and so on.

Some difficulty had been anticipated in keeping the capillary of the viscometer clean. The method of washing with a few drops of water cannot be used in ternary systems of the present type, since the addition of water in large excess to most of the saturated solutions results in the precipitation of neutral or basic salts. In the present work, a dilute solution of arsenic acid was found quite satisfactory as a wash liquid, and a few drops of this were blown down the viscometer from a wash-bottle every time the composition of the mixture was changed. Such a procedure was neither permissible nor necessary in order to obtain concordant results for successive readings of the same equilibrium. In order to provide for cases in which suitable wash liquids cannot be found for a ternary system, the author has devised an apparatus in which the stirrer and viscometer are separate, the latter being instantly removable for cleaning without disturbing the rest of the apparatus. So far, however, it has been found quite unnecessary to use it. Moreover, in ternary systems the temperature is kept constant, and consequently crystallisation in the capillary through temperature changes cannot occur. When readings are being taken with the viscometer, it is essential that the air expelled from the solubility tube by the falling liquid should be able to escape easily. In the previous work, the stirrer bearing provided an adequate leak, but in the present case it was found necessary to remove the glass plug from the tube, F (Fig. 1). When equilibrium was established the readings agreed to within 0·4 sec., and frequently to within 0·2 sec. The agreement is closer than in the previous work, but the percentage error remains about the same.

The analysis of the phase samples was effected as follows. The arsenic was separated by reduction with hydrazine and subsequent distillation as arsenious chloride. The apparatus used was that described by Jannasch and Seidel (*Ber.*, 1910, **43**, 1218), with the addition that the receiver was cooled in a large beaker of water and was furnished with a water trap to prevent any escape of arsenic. (These precautions are, however, probably unnecessary.) An aliquot part of the phase sample solution was measured into the distillation flask, concentrated hydrochloric acid was added until the volume was about 110 c.c., and the solution was saturated with hydrogen chloride; 3 g. of hydrazine sulphate and 1 g. of potassium bromide were then added, and the liquid was distilled until only 30—40 c.c. remained. The distillate was titrated as described below. High results are obtained unless the flame is screened from all but the bottom of the flask by an asbestos ring with a wire gauze centre: without this precaution, the flask becomes heated above the liquid and hydrazine distils over. The amount of arsenic in the reagents was found to be negligible. The use of a continuous stream of hydrogen chloride during the distillation was found, in agreement with Jannasch and Seidel, to be quite unnecessary for the complete volatilisation of the arsenic.

The distillate was titrated with potassium iodate solution, according to the method described in Scott's "Standard Methods of Chemical Analysis," 1922, Vol. I, p. 44. The iodate solution was standardised against resublimed A.R. arsenious oxide (B.D.H.). Owing to the distillation, the arsenious chloride solution was more dilute than is usual in this titration, and the reaction was consequently slower; it was therefore necessary to add the last few c.c. of the iodate very cautiously, waiting 5 minutes between each addition. As a check, the solution was titrated back with a standard arsenite solution, but the first drop almost invariably restored the colour to the chloroform.

The iron in the liquid phase was determined colorimetrically with ammonium thiocyanate—it never exceeded 0·1% as Fe_2O_3. In the solid phases, it was determined either (1) gravimetrically as oxide in the residue from the arsenic distillation, after decomposing the excess of hydrazine with nitric acid; (2) by titration of the residue with potassium dichromate, after removing the hydrazine with nitric acid and expelling the latter by evaporation; or (3) by direct titration of the phase sample solution with potassium dichromate. Stannous chloride was used as a reducing agent in the dichromate titrations. Methods (1) and (2) were both unsatisfactory because the weights of iron in the quantities of solution necessary to obtain a convenient amount of arsenious chloride were small. By using method (3) more solution could be titrated, and it was found by experiment that, provided the concentration of hydrochloric acid was not too high, the presence of the small amounts of arsenate involved did not appreciably affect the results. To ensure that the hydrochloric acid concentration was sufficiently low, the phase sample solutions were diluted with water before reduction by the stannous chloride, until in the cold the colour due to the ferric chloride was a pale yellow.

Results.

The results are in Table I. The composition of the phases is expressed in terms of Fe_2O_3 and As_2O_5, and, in the case of mixtures 1—13, as $FeAsO_4$ and H_3AsO_4 also. This second mode of expression is made possible by the absence of basic solid phases, and its object is to bring out more clearly the orientation of the conjugation lines when the results are plotted. If Fe_2O_3 and As_2O_5 are used as plotting components, the diagram is confined within an area which is very narrow in the direction $Fe_2O_3 \longleftrightarrow As_2O_5$, and its significance is difficult to appreciate. Mixtures 14—20 are not so treated because their percentages of Fe_2O_3 in the liquid phase were only determined approximately. Graphic expression is, however, not

TABLE I.

(Solid phase analyses marked with an asterisk refer to the *dried* solid, the remainder to the moist solid.)

		Liquid phase.				Solid phase.			
Mixture.	Time of flow (secs.).	% Fe_2O_3.	% As_2O_5.	% $FeAsO_4$.	% H_3AsO_4.	% Fe_2O_3.	% As_2O_5.	% $FeAsO_4$.	% H_3AsO_4.
1	81·7	Trace.	2·6	Trace.	3·2	10·3	17·0	25·1	2·7
2	82·6	,,	3·5	,,	4·3	10·8	18·2	26·3	3·3
3	83·4	,,	4·4	,,	5·4	9·6	17·1	23·4	4·1
4	84·5	,,	5·4	,,	6·7	13·7	23·3	33·4	4·45
5	85·0	,,	5·8	,,	7·2	10·9	20·9	26·6	6·4
6	85·7	,,	6·4	,,	7·9	15·8	27·9	38·5	6·4
7	86·6	0·001	7·96	0·001	9·83	—	—	—	—
8	89·0	0·004	10·11	0·01	12·47	4·1	15·2	10·0	11·5
9	92·1	0·01	12·49	0·02	15·40	5·5	18·74	13·4	13·4
10	97·4	0·036	16·19	0·088	19·93	—	—	—	—
11	102·0	0·037	18·82	0·090	23·17	2·7	21·22	6·6	21·41
12	108·0	0·059	21·77	0·14	26·78	3·4	24·94	8·3	24·75
13	110·6	0·076	23·13	0·185	28·42	26·8*	52·8*	65·4*	17·5*
14	87·4	Approximately 0·1	8·0			—	—		
15	87·4		8·4			—	—		
16	92·6		12·3			21·8*	58·6*		
17	94·1		13·2			—	—		
18	95·5		14·3			—	—		
19	96·7		14·9			—	—		
20	97·7		15·5			22·5*	57·9*		

Composition and Appearance of Solid Phases.—Mixtures 1—10 : Fe_2O_3,As_2O_5,xH_2O, with adsorbed acid. Amorphous.

Mixtures 11—13 : Fe_2O_3,As_2O_5,xH_2O (with adsorbed acid) + $Fe_2O_3,2As_2O_5,8H_2O$. Amorphous and needles.

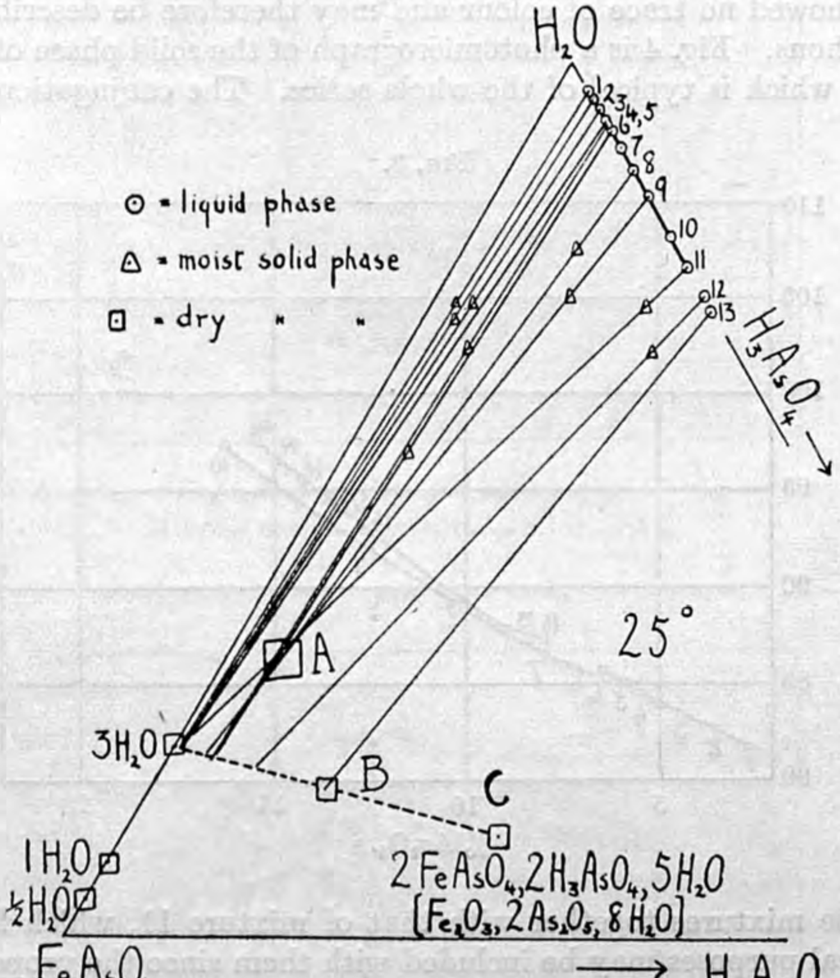
Mixtures 14—20 : $Fe_2O_3,2As_2O_5,8H_2O$ (Calc. : Fe_2O_3, 20·94; As_2O_5, 60·21%). Needles.

so necessary for those mixtures, for the compositions of their solid phases were found by analysis of the dried solid. Fig. 2 shows mixtures 1—13 plotted on a triangular diagram, and Fig. 3 shows the times of flow of the liquid phases (excluding mixture 13) plotted against their content of As_2O_5.

From Table I, it is seen that the percentage of ferric oxide in all the liquid phases is extremely small : even mixtures 14—20 which are metastable show only about 0·1%. It was feared at first that this small solubility would render the viscosity measurements useless through their not differing appreciably from those of aqueous arsenic acid solutions. The curves in Fig. 3 show, however, that mixtures 14—20 have a distinctly higher viscosity than the others at the same acid concentrations ; on the assumption that the viscosity increases with solubility, this confirms the metastability of these mixtures. Further, a distinct break occurs between mixtures 6 and 7, the significance of which is discussed later.

From Table I it will be seen that the mixtures 11—13 possessed the same two solid phases. It is evident that in these cases equilibrium was not attained, since theory demands that there shall be only one composition for a solution in equilibrium with any two

FIG. 2.



solid phases at constant temperature. This is not to be attributed to any failure to take the usual precautions to ensure the attainment of equilibrium, for the stable solid phase was presumably present in each case, and stirring was continued long after any change in the viscosity of the solution and in the appearance of the solid under the microscope had ceased (the mixtures were stirred for 35, 6, and 26 days, respectively). Rather must it be ascribed to an extreme sluggishness in approaching equilibrium. This was also experienced in the ferric phosphate work in this region, and is no doubt due to the low solubility of the solid phases. In view of this, it is impossible to be certain to what extent equilibrium was reached in the other mixtures. The least doubt would appear to attach to mixtures 14—20 which possessed a single well-defined crystalline solid phase. These, however, were metastable.

The solid phase of mixtures 1—10 was seen under the microscope to be very finely divided, the average diameter of the particles being 1·0—1·5 μ. Under crossed Nicols and an oil-immersion objective they showed no trace of colour and may therefore be described as amorphous. Fig. 4 is a photomicrograph of the solid phase of mixture 1 which is typical of the whole series. The conjugation lines of these mixtures together with that of mixture 11, which for all practical purposes may be included with them since the proportion of acid salt which it contained was exceedingly small, suggest (see Fig. 2) that the solid is a neutral ferric arsenate containing varying amounts of adsorbed arsenic acid. In this respect the system is similar to the ferric phosphate system (*loc. cit.*). Marked adsorption is indeed to be expected in these cases, for the solid is finely divided and amorphous. This factor limits the value of any conclusions drawn from the conjugation lines, and further evidence is necessary to show where they end. In the present case an attempt to provide this was made by analysing the dried solid phase of mixture 13 (point B). This contained both the neutral arsenate and the acid salt $Fe_2O_3,2As_2O_5,8H_2O$ (point C), so that extrapolation of the line

FIG. 3.

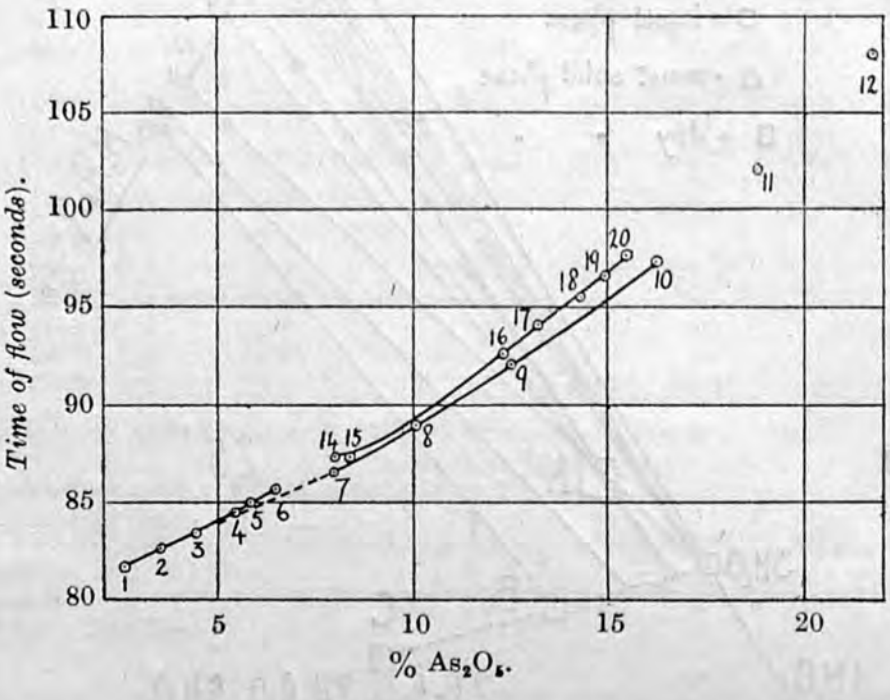
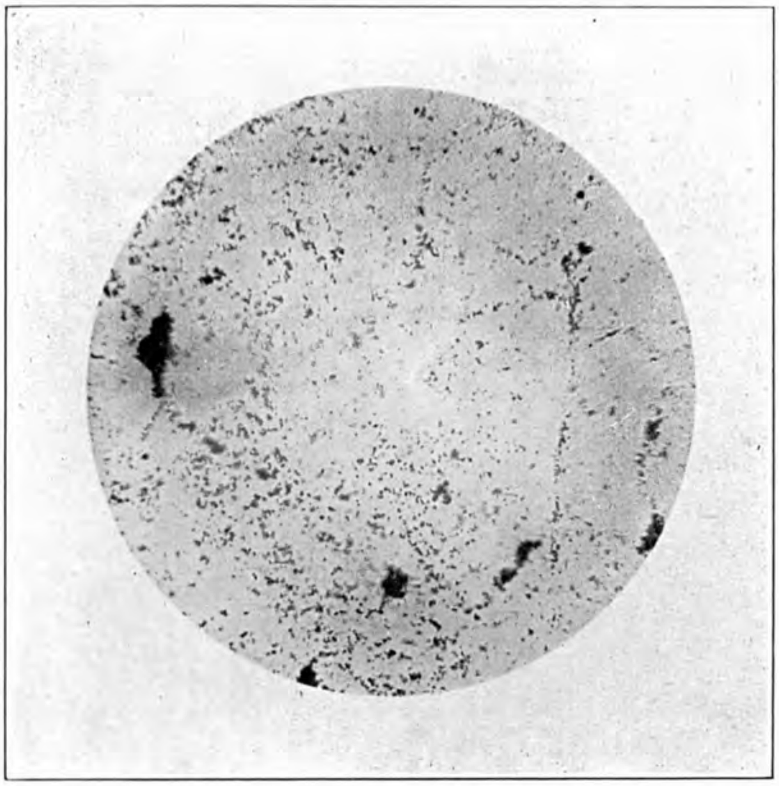


FIG. 4.



Fe_2O_3,As_2O_5,xH_2O *and adsorbed acid.*
Average diameter of particles : 1·0—1·5 μ.

FIG. 5.

$Fe_2O_3,2As_2O_5,8H_2O$.
(× 260).

[*To face p.* 1766]

CB gives information as to the water content of the former. As will be seen from the figure, this leads to the composition

$$FeAsO_4,3H_2O \text{ (or } Fe_2O_3,As_2O_5,6H_2O\text{)}.$$

No great reliance can, however, be placed on the accuracy of the determination of the point B, since it is probable that the solid suffered some change in composition during the drying process on account of its fine state of division and the presence of adsorbed acid. (The solid was washed with anhydrous ether which was then removed in a current of dry air.)

It will be noticed that the lines fall into two groups, *viz.*, 1—4 and 5—11, the latter converging approximately on the point A. It does not appear, however, that this has any significance, for the point A is far removed from the line CB, and, moreover, no simple formula can be assigned to it. The break in the viscosity curve between mixtures 6 and 7 (see Fig. 3) may be due to a small change in the solid phase, but it is more probably due to incomplete attainment of equilibrium, especially as the order in which the mixtures were prepared was from Nos. 6 to 1 followed by a reversion to No. 7, *i.e.*, to the mixture on the other side of the break. Possibly the true course of the curve is as represented by the broken line drawn from 3 to 7.

If the conjugation lines reach as far as the line CB produced, the diagram shows that certain of them cross over the others. This, too, indicates that equilibrium was not attained, for it implies that a mixture of the three components lying within the crossing region has a choice of equilibrium states. A similar arrangement of lines was observed in the ferric phosphate work at 25° (*loc. cit.*, p. 2226), but its significance was not then appreciated. For the present, the solid phase in equilibrium with mixtures 1—10 is described as Fe_2O_3,As_2O_5,xH_2O (where x is probably not far removed from 6), containing adsorbed acid.

Mixtures 14—20 were made by stirring another portion of the starting material with arsenic acid solutions of progressively decreasing strengths. They were all metastable, as both the analyses and the viscosity curves show. The solid consisted of small needle-shaped crystals (see photomicrograph, Fig. 5) which could be easily filtered; they were dried by washing with ether and underwent no visible change. They were therefore analysed dry in two cases and the results are given in Table I. From these figures and from the crystalline form, it was concluded that they were $Fe_2O_3,2As_2O_5,8H_2O$, isomorphous with $Fe_2O_3,2P_2O_5,8H_2O$ (*loc. cit.*, p. 2230). The analytical figures are not as close to this composition as is desirable, but they do not agree with any other known or anticipated compound. The inaccuracy is probably due to the smallness of the crystals, the relatively large surface magnifying the effect of incipient decomposition. The error is in the basic direction, which is in agreement with this explanation. This compound does not appear to have been described before. Its constitution and that of its phosphate analogue cannot be explained in any simple manner on the assumption that the salts are formed simply by the replacemen of acid hydrogen by ferric iron. This is further evidence that the salts are complex. A formula analogous to that given by Weinland and Ensgraber to the phosphate would serve also for the arsenate, *viz.*, $[Fe(AsO_4)_2]H_3,2{\cdot}5H_2O$. No sign of Metzke's compound, $2Fe_2O_3,3As_2O_5,22{\cdot}5H_2O$, has been found.

Summary.

The system ferric oxide–arsenic acid–water has been studied between the concentrations 2·6 to 23·13% of As_2O_5 at 25°. Within this range the following solid phases have been found : The neutral salt, Fe_2O_3,As_2O_5,xH_2O (where x is probably not far removed from 6), carrying varying amounts of adsorbed arsenic acid; and the acid salt, $Fe_2O_3,2As_2O_5,8H_2O$, which has apparently not been described before. No basic salts were obtained. A feature of the system was the sluggishness with which equilibrium was approached even in the presence of the stable phase, and it is evident that in some cases it was not attained.

The author's stirrer-viscometer was used in this work in order to test its usefulness in the investigation of ternary systems. No difficulty was experienced in obtaining readings concordant to within 0·5% and frequently less. The system did not, however, afford much opportunity for making use of viscosity measurements.

In conclusion, the author wishes to express his thanks to Dr. J. F. Spencer for his helpful interest in this work.

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[*Received, April 2nd,* 1927.]

Printed in Great Britain by Richard Clay & Sons, Limited,
Bungay, Suffolk.