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

By NORMAN HOLT HARTSHORNE.

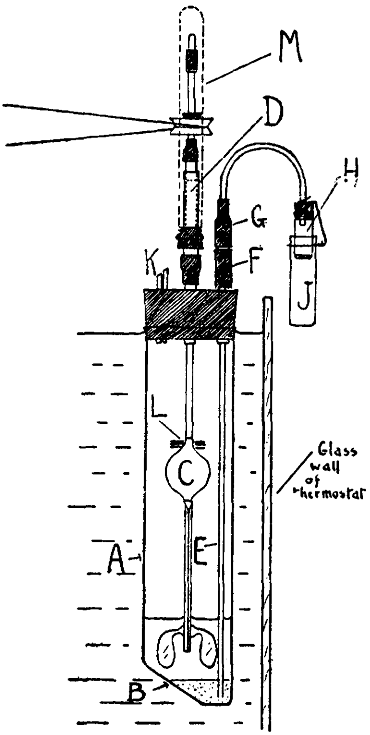
THIS work was undertaken (*a*) to discover whether any of the numerous ferric arsenates described in the literature were merely stages in a series of adsorption compounds, as in the case of the ferric phosphates (Carter and Hartshorne, J., 1923, **123**, 2223); and (*b*) to test the usefulness of the 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 Simek (*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.

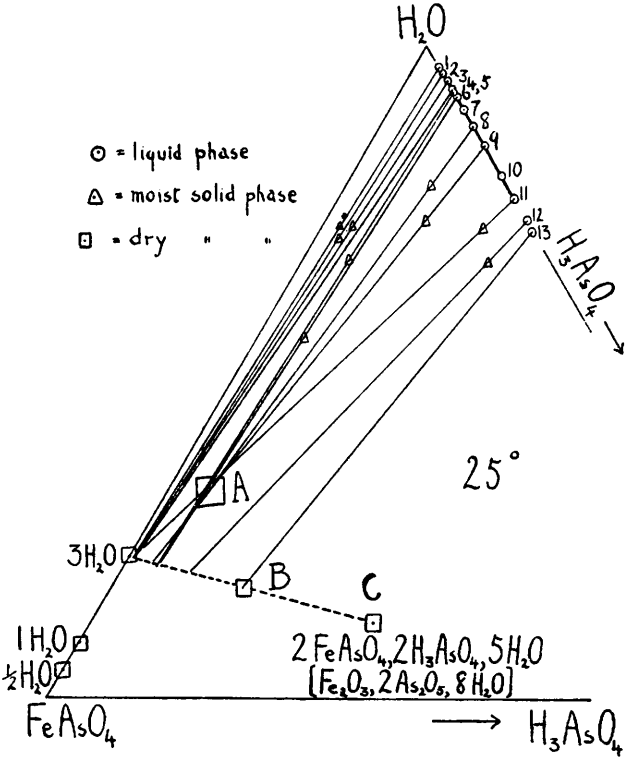
Mixtures 14—20: $Fe_2O_3,2As_2O_5,8H_2O$ (Calc.: Fe_2O_3, 20·94; As_2O_5, 60·21%). Needles.

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 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

FIG. 2.



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.

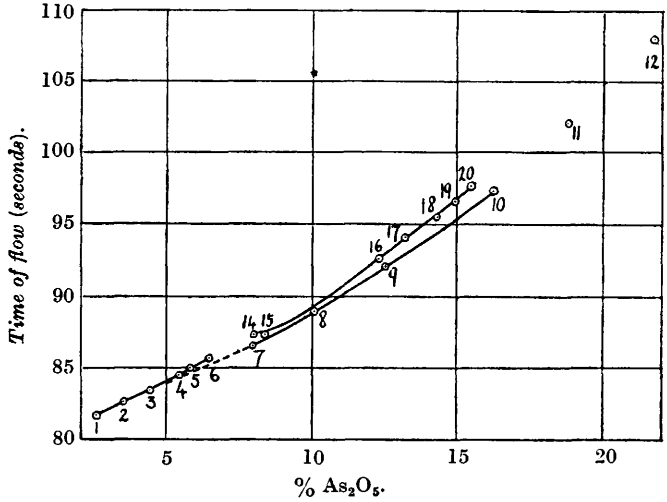
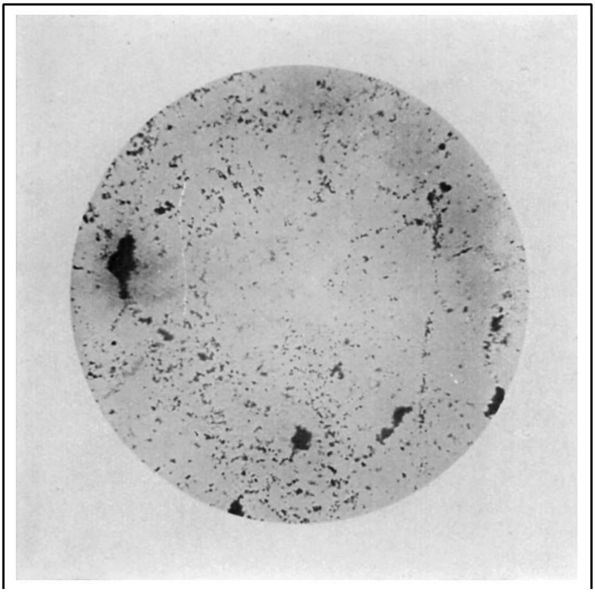
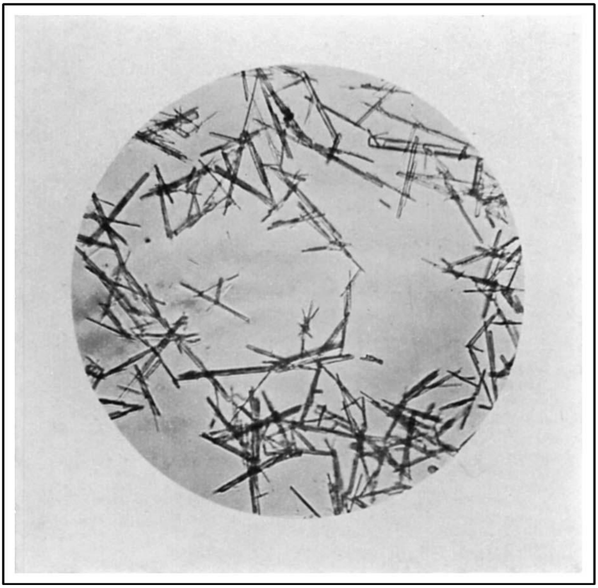


FIG. 4.



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).

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

$FeAsO_4,3H_2O$ (or $Fe_2O_3,As_2O_5,6H_2O$).

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 replacement 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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