633. *Complexes involving Tervalent Iron and Orthophosphoric Acid. Part V.* Magnetic Susceptibility Measurements on Iron*(III) *Solutions containing Orthophosphate.*

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The results of magnetic susceptibility measurements on iron(III) solutions containing phosphoric acid have shown that the lowering of magnetic moment observed by previous workers is dependent on the mole ratio of PO_4 : Fe in the solution. The moment is lowest for solutions in which the PO_4 : Fe mole ratio is 1 : 2 and the low values are attributed to the formation of polynuclear ions, evidence for the formation of which has been provided by ion-exchange experiments (Part IV *). From the present results it is evident that appreciable concentrations of such complexes may be formed under optimum conditions.

THE magnetic moments of iron(III) in perchlorate solutions with and without addition of phosphate were measured by Werbel, Dibeler, and Vosbourgh [1] who observed a decrease in moment in the presence of phosphate. This observation was of interest in connection with present work on ferric phosphate complexes and a more extensive study has been made of the magnetic properties of solutions containing iron(III) and orthophosphate.

Magnetic measurements have now been made on solutions of ferric phosphate in phosphoric acid, with and without addition of perchloric and hydrochloric acids, and on solutions of ferric perchlorate, chloride, and sulphate, in each case with and without addition of phosphoric acid. As a result the conditions under which a decrease in moment occurs have been established and an explanation of the phenomenon is offered.

EXPERIMENTAL and RESULTS

Magnetic susceptibilities were determined at room temperature by use of a Gouy-type magnetic susceptibility balance. Calibration was effected as previously described [2] and was checked by measurements on solutions of chrome alum, cobalt sulphate, etc. Diamagnetic corrections were derived from measurements on solutions containing calcium or potassium ions

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* Part IV, *J.*, 1957, 959.

[1] Werbel, Dibeler, and Vosbourgh, *J. Amer. Chem. Soc.*, 1943, **65**, 2329.

[2] Clark, Curtiss, and Odell, *J.*, 1954, 63.

in place of iron(III) ions (at the same molar concentration) but otherwise identical with the test solutions.

Ferric phosphate was prepared[3] from analytical-grade reagents. Solutions of ferric perchlorate were obtained by the sorption of iron from ferric chloride solution on cation-exchange resin Zeo-Karb 225, followed (after the column had been thoroughly washed) by elution with perchloric acid solutions. The iron-rich fraction of the effluent was recycled through the column after this had been reloaded with iron and washed again. For this purpose,

TABLE 1. *Magnetic susceptibilities for solutions of ferric phosphates in phosphoric acid, in presence and in absence of other acids.*

Mole ratios in solution Fe : PO_4 : X	Temp., ° K	$10^5\chi_{Fe(III)}$	$\mu_{eff.}$
(*a*) No other acid present, 0·267 mole of Fe/kg.			
1 : 7·19 : —	292	1498	5·92
1 : 9·78 : —	292	1492	5·91
1 : 12·42 : —	293	1486	5·91
1 : 14·91 : —	293	1492	5·92
(*b*) X = ClO_4, 0·265 mole of Fe/kg.			
1 : 7·43 : 1·02	293	1485	5·90
1 : 7·43 : 3·42	293	1484	5·90
1 : 7·43 : 4·52	293	1493	5·92
1 : 7·43 : 6·80	293	1485	5·90
(*c*) X = Cl, 0·274 mole of Fe/kg.			
1 : 7·43 : 1·04	291·5	1493	5·90
1 : 7·19 : 2·08	291·5	1497	5·91
1 : 7·19 : 4·07	291·5	1499	5·92
1 : 7·19 : 6·29	291·5	1514	5·94

TABLE 2. *Magnetic susceptibilities for solutions of ferric salts with and without added phosphoric acid.*

(*a*) X = ClO_4, 0·267 g. atom of Fe/kg.

Mole ratio	Fe ...	1	1	1	1	1	1	1	1	1
	X ...	3·19	3·19	3·19	3·19	3·19	3·19	3·19	3·19	3·39
	PO_4 ...	0	0·39	0·74	1·12	1·48	2·20	2·94	3·68	0
pH		0·85	—	0·05	—	—	—	—	—	—
Temp., ° K		288	290	288	290	288	288	288	288	290
$10^5\chi_{Fe(III)}$		1482	1253	1268	1361	1420	1464	1452	1447	1487

(*b*) X = Cl, 0·270 g. atom of Fe/kg.

Mole ratio	Fe ...	1	1	1	1	1	1
	X ...	3·10	3·10	3·10	3·10	3·10	3·10
	PO_4 ...	0	0·38	0·74	1·11	1·47	2·17
pH		1·48	0·61	0·47	0·40	0·35	0·31
Temp. ° K.		294	294	294	294	294	294
$10^5\chi_{Fe(III)}$		1503	1261	1278	1336	1366	1405

(*c*) X = Cl, 0·256 g. atom of Fe/kg.

Mole ratio	Fe ...	1	1	1	1	1	1
	X ...	3·96	3·96	3·96	3·96	3·96	3·96
	PO_4 ...	0	1·06	2·26	3·54	5·51	7·74
Temp., ° K.		291·5	291·5	292	292	292	292
$10^5\chi_{Fe(III)}$		1500	1500	1500	1498	1504	1493

(*d*) X = SO_4, 0·270 g. atom of Fe/kg.

Mole ratio	Fe ...	1	1	1	1	1	1	1	1	1	1
	X ...	1·92	1·92	1·92	1·92	1·92	1·92	1·92	1·92	2·27	2·46
	PO_4 ...	0	0·37	0·73	1·11	1·45	2·20	2·91	3·64	0	0
pH		0·90	—	0·52	—	0·42	0·36	0·30	0·26	—	—
Temp., ° K.		288	291	288	291	288	288	288	288	291	291
$10^5\chi_{Fe(III)}$		1421	1277	1334	1377	1420	1433	1464	1468	1432	1437

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[3] Salmon, *J.*, 1952, 2316.

as in the preparation of all other solutions, analytical grade reagents were used. We were unable to obtain solutions of ferric perchlorate free from chloride impurity by the method used by Werbel, Dibeler, and Vosbourgh.[1] pH was measured as before.[4]

The iron content (2% w/w approx.) of the stock solutions, from which the solutions for magnetic measurements were prepared, was determined by a standard volumetric procedure and total anion concentration (apart from phosphate which was determined gravimetrically) was estimated by a cation-exchange method.[5] Solutions for the measurements were obtained by mixing 15 g. of stock solution with 5 g. of water or of acid solution.

Measurements on Ferric Phosphate Solutions.—In these solutions the mole ratio of $PO_4 : Fe$ was of necessity high, because of the low solubility of ferric phosphate in dilute phosphoric acid solutions. Table 1 shows that in them and in their mixtures with phosphoric, perchloric, and hydrochloric acids, the effective magnetic moment is approximately 5·90 Bohr magnetons.

Measurements on Ferric Perchlorate, Chloride, and Sulphate Solutions.—The values of $\chi_{Fe(III)}$ found for the ferric chloride solutions (Table 2 *b, c*) are close to those for the ferric phosphate solutions (Table 1), whilst those for ferric perchlorate and sulphate are rather lower, but are raised on addition of free perchloric or sulphuric acids, respectively (Table 2 *a, d*), as observed by Bose.[6]

In the absence of much free acid in the initial solutions, additions of phosphoric acid to all three solutions cause, initially, a very sharp fall in the values of $\chi_{Fe(III)}$ which, however, pass through a minimum value and rise again to the initial values in the presence of excess of phosphoric acid (Table 2 *a, b, d*)—as would be expected from the preceding experiments (Table 1). In the presence of much free acid, however, the fall in $\chi_{Fe(III)}$ is not observed (Table 2 *c*).

DISCUSSION

It is evident that in solutions containing much free acid there is no significant deviation from a magnetic moment corresponding to five unpaired electrons for the iron(III) atoms (Tables 1 and 2 *c*). Now there is evidence to indicate that in solutions of ferric phosphate in phosphoric acid (cf. Table 1 *a*) complexes such as $[Fe(HPO_4)_3]^{3-}$ are present.[3, 7] Hence, it can be deduced that in such complexes the iron(III) atoms have five unpaired electrons—as might be expected from the electronegative character of the ligand. The same can be expected for other mononuclear complexes such as $[FeHPO_4]^+$.[8]

From the values of $\mu_{eff.}$ shown in the Figure it appears that, for solutions containing less free acid, a minimum in the moment is found for those containing phosphate and iron in mole ratios close to 1 : 2, regardless of the other anions present (perchlorate, chloride, or sulphate). A value of 5·3 B.M. or possibly much less can be deduced by extrapolation for solutions having this mole ratio; since in this region the apparent change in mass measured on application of the field was barely greater than the diamagnetic correction, it is difficult to obtain more precise values. The facts that this minimum occurs at, or close to, a mole ratio of $PO_4 : Fe = 1 : 2$ and that the effective magnetic moment changes so markedly with small variations in that ratio indicate that an interaction between ferric ions and phosphate ions is involved and that a complex of the type $[Fe_2(PO_4)]^{3+}$ is formed. Further support for this conclusion has been provided by ion-exchange studies.[9] In these, polynuclear complexes of this type are formed in solutions containing low concentrations of free acid, but are decomposed in solutions of higher acidity to yield complexes such as $[FeHPO_4]^+$. The reason for the absence of any change in moment in the presence of excess of free acid (Table 2 *c*) thus becomes apparent.

The lower magnetic moment associated with the formation of an ion such as

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[4] Genge and Salmon, *J.*, 1957, 256.

[5] Samuelson, " Ion Exchangers in Analytical Chemistry," John Wiley & Sons Inc., 1953, pp. 117 *et seq.*

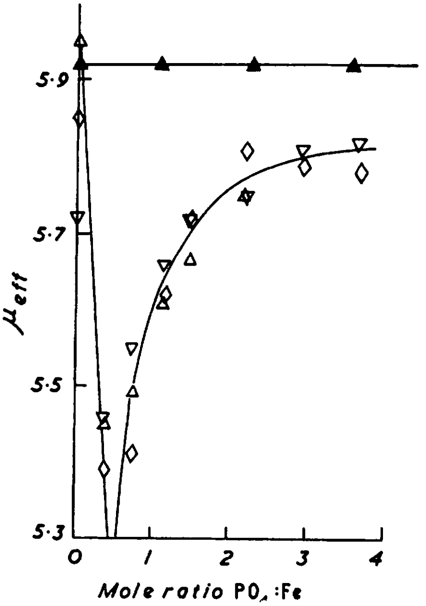
[6] Bose, *Proc. Indian Acad. Sci.*, 1935, *A*, **1**, 754.

[7] Jameson and Salmon, *J.*, 1954, 28.

[8] Salmon, *J.*, 1953, 2644.

[9] Holroyd and Salmon, *J.*, 1957, 959.

$[Fe_2(PO_4)]^{3+}$ is presumably due to the same interaction resulting from the close proximity of two iron(III) atoms as occurs in the diamagnetic $[Fe_2(OH)_2]^{4+}$ dimer.[10] However, a study of scale models shows that in such an ion the iron atoms are not necessarily held in close proximity, but are free to take up positions in which interaction between their unpaired electrons is unlikely to occur. It is possible, however, that the phosphate-containing ion is derived from the $[Fe_2(OH)_2]^{4+}$ ion, by replacement of one hydroxyl group by a phosphate group to give an ion such as $[Fe_2(OH)(HPO_4)]^{3+}$ or $[Fe_2(OH)(PO_4)]^{2+}$.



Values of $\mu_{eff.}$ *for* Fe^{3+} *in mixtures of solutions of* Fe(III) *salts with orthophosphoric acid solutions.*

△ $FeCl_3$ (low free acid).
▲ $FeCl_3$ (high free acid).
▽ $Fe_2(SO_4)_3$.
◊ $Fe(ClO_4)_3$.

Such formation, which appears feasible from a study of scale models, agrees with the results of the ion-exchange experiments.[9]

Such ions as $[Fe_2(OH)(HPO_4)]^{3+}$ or $[Fe_2(OH)(PO_4)]^{2+}$ would presumably be diamagnetic and hence their formation from Fe^{3+} ions would be accompanied by a big change in moment. Nevertheless, the very rapid fall in $\mu_{eff.}$ as a 1 : 2 mole ratio of PO_4 : Fe is reached indicates that in such solutions a significant concentration of these complexes is formed—a conclusion which finds support since in these solutions (in which the mole ratio is 1 : 2) the dark yellow of the original ferric salt solutions has almost entirely disappeared.

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[10] Mulay and Selwood, *J. Amer. Chem. Soc.*, 1955, **77**, 2693.