[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

x-Ray Studies on the Hydrous Oxides. V. Beta Ferric Oxide Monohydrate

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When aqueous solutions of ferric chloride that are not too dilute are allowed to stand for a long time at room temperature or are heated slowly to 60–100°, they deposit a yellow hydrous precipitate containing an amount of chloride which varies with the conditions of formation.

x-Ray diffraction examination by Böhm[1] in Haber's laboratory of the yellow precipitate from a sol aged for twenty years showed it to be distinct from α- or γ-Fe_2O_3 and from α- or γ-$Fe_2O_3 \cdot H_2O$. Schikorr[2] pointed out that the precipitate obtained by heating slowly to 90° a solution of 35 g. of $FeCl_3 \cdot 6H_2O$ in one liter of water, gave an x-ray diffraction pattern identical with Böhm's preparation and different from Stirnemann's[3] definite FeOCl. Böhm was convinced that his preparation was a basic salt but both Schikorr[2] and Heller and Zocher[4] were in doubt as to whether the yellow precipitate was really a definite basic chloride.

Fischer[5] and Schikorr[2] observed a loss of approximately one mole of water per mole of ferric oxide on dehydrating the yellow precipitate obtained by slow hydrolysis of ferric chloride. In the absence of x-ray diffraction data, Fischer did not know that this yellow compound was different from other yellow oxides of iron.

The view that the yellow precipitate under consideration is a basic chloride rather than a ferric oxide or oxide hydrate is open to question since the Fe : Cl ratio is not constant but depends upon the conditions of formation. The Fe : Cl ratio of the alleged basic salt has been given at various times such values as: 2.33,[6] 4.5,[7] 6.33;[8] 6.67,[9] 7,[10] 8.[2,11] These values are purely accidental as evidenced by the data given in the experimental portion of this paper.

Experimental

Method of Formation.—The conditions of forming the yellow compound are illustrated by the following experiments: 100-cc. portions of freshly prepared ferric chloride solutions were placed in 125-cc. flasks with reflux condensers attached, and heated to boiling during a period of forty-five minutes. The results are summarized in Table I. In every case the final product is a brick-red precipitate. In all cases except the most dilute solutions a yellow sol or yellow precipitate was formed as an intermediate product between the solution and the brick-red precipitate. Fifteen years ago in the absence of x-ray diffraction data, one of us[12] concluded that the yellow product formed by slow hydrolysis was a hydrous ferric oxide which differed from the brownish-red ferric oxide gel and the brick-red precipitate only in particle size and physical structure. The primary particles of the yellow product were believed to be larger and less hydrous than the

TABLE I

HYDROLYSIS OF FERRIC CHLORIDE SOLUTIONS

$FeCl_3$, M	Color of solution	Color of precipitate (or sol)		
		1 hour	2 hours	3 days
0.01	Yellow	Clear red (sol)	Clear red (sol)	Brick-red
.02	Yellow	Clear red (sol)	Red (sol)	Brick-red
.03	Yellow	Clear red (sol)	Reddish-yellow (sol)	Brick-red
.04	Yellow	Clear red (sol)	Yellow (sol)	Brick-red
.05	Yellow	Yellow	Yellow	Brick-red
.25	Yellowish-brown	Yellow	Yellow	Brick-red
.50	Reddish-brown	Yellow	Yellow	Brick-red
.75	Reddish-brown	Yellow	Yellow	Brick-red
1.00	Reddish-brown	Yellow	Yellow	Brick-red

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[1] Böhm, *Z. anorg. allgem. Chem.*, **149**, 210 (1925).

[2] Schikorr, *Kolloid-Z.*, **52**, 25 (1930).

[3] Stirnemann, *Neues Jahrb. Mineral.*, **52A**, 334; **53A**, 59 (1925); *cf.* Bauer, *Z. Elektrochem.*, **32**, 428 (1926); *cf.* Goldsztaub, *Compt. rend.*, **198**, 667 (1934).

[4] Heller and Zocher, *Z. physik. Chem.*, **166**, 365 (1933).

[5] Fischer, *Z. anorg. allgem. Chem.*, **66**, 37 (1910).

[6] Wittstein, *Chem. Zentr.*, **15**, 862 (1844).

[7] Ordway, *Am. J. Sci.*, [2] **26**, 197 (1858); Béchamp, *Ann. chim. phys.*, [3] **57**, 296 (1859).

[8] *Cf.* Picton and Linder, *J. Chem. Soc.*, **61**, 153 (1892).

[9] Britton, *ibid.*, **127**, 2148 (1925).

[10] Bary, *Rev. gén. colloïdes*, **6**, 209 (1928); *Compt. rend.*, **187** 538 (1928).

[11] Pickering, *J. Chem. Soc.*, **105**, 472 (1914).

[12] Weiser, *J. Phys. Chem.*, **24**, 277 (1920).

TABLE II

PREPARATIONS OF VARYING CHLORIDE CONTENT

	Preparation and treatment	%, HCl	Ratio Fe:Cl
A	4 liters of 0.1 *M* $FeCl_3$ heated to 95° (6 hr.) and digested 24 hours. Precipitate washed once with 250 cc. water; dried at 60°	7.76	4.79
B	1 liter of 0.1 *M* $FeCl_3$ heated slowly to 95° (3 hr.). Precipitate washed once with water and 8 times with 50-cc. portions of acetone; dried at 150°	5.8	6.4
C	1 liter of 0.4 *M* $FeCl_3$ heated to 90° (3 hr.) and digested 12 hours. After decanting the supernatant liquid, water was added and the mixture dialyzed at 90° changing the water continuously		
	(a) Two weeks' dialysis; sample dried at 71°	3.52	10.96
	(b) Three weeks' dialysis; sample dried at 110°	2.99	..
	(c) Eight weeks' dialysis; sample dried at 110°	3.04	..
D	1 liter of 0.17 *M* $FeCl_3$ and of 0.33 *M* $FeCl_3$ heated slowly to 90° (3 hr.). Precipitate washed once with water and 6 times with 150 cc. portions of dilute ammonia		
	(a) From 0.17 *M* $FeCl_3$; sample dried at 120°	1.87	..
	(b) From 0.33 *M* $FeCl_3$; sample dried at 120°	1.44	..
	(c) From 0.33 *M* $FeCl_3$; sample dried at 92°	1.39	28.0
E	4 liters of 0.1 *M* $FeCl_3$ heated slowly to 65° (3 hr.) and digested 24 hours. Precipitate washed by decantation; twice with 3-liter portions of water and 20 times with 12-liter portions of dilute ammonia. Sample dried at 30° in air	0.87	37.8
F	4 liters of 0.1 *M* $FeCl_3$ heated slowly to 70° (6 hr.) and digested 20 hours. Precipitate washed by decantation; twice with 3-liter portions of water; 11 times with 12-liter portions of dilute ammonia; and twice with 12-liter portions of water. Sample dried at 101°	0.90	45.0

particles in the brownish-red gel and smaller and more hydrous than the particles in the brick-red precipitate. It is now known, however, that the aged brown gel and the red precipitate are hydrous α-Fe_2O_3 whereas the yellow product is a third polymorphic modification of ferric oxide monohydrate.

Samples of the yellow compound were prepared for x-ray analysis and isobaric dehydration experiments. The method of preparation, treatment and chloride content of these samples are summarized in Table II.

x-Ray Analysis.—The various samples listed in Table II were found to give identical x-radiograms. Since the chloride content of the samples varies from 7.76% to but 0.87%, it is apparent that chloride is not an essential constituent of the crystal lattice of the compound. The x-ray data are given in Table III and the diagram of a typical pattern labeled β-$Fe_2O_3 \cdot H_2O$ is shown in Fig. 1. For purposes of comparison the diffraction patterns for α- and γ-Fe_2O_3 and for α- and γ-$Fe_2O_3 \cdot H_2O$ are included in the figure. There can be no doubt of the chemical individuality of the yellow precipitate formed by the hydrolysis of ferric chloride. It is apparent that the samples contain little or no "amorphous" ferric oxide. This is especially true for the samples dialyzed in the hot since under these conditions, any "amorphous" oxide would be expected to age rapidly to α-Fe_2O_3 which would show up in the x-radio-

TABLE III

x-RAY DIFFRACTION DATA FOR β-$Fe_2O_3 \cdot H_2O$

	Interplanar spacings in Ångström units					Estd. rel. intensity
		Observed for different samples				
hkl	Calcd.	1	2	3	4	
100	5.280	5.3	5.4	5.4	5.3	4
001	3.340	3.34	3.33	3.30	3.31	8
200	2.640	2.63	2.63	2.63	2.62	4
040	2.560	2.56	2.54	2.54	2.53	10
031	2.298	2.31	2.28	2.28	2.28	2
221	1.950	1.953	1.945	1.943	1.941	7
300	1.760	1.760	1.751	1.750	1.745	2
012	1.612	1.644	1.640	1.630	1.635	8
132	1.418	1.448	1.444	1.436	1.440	1

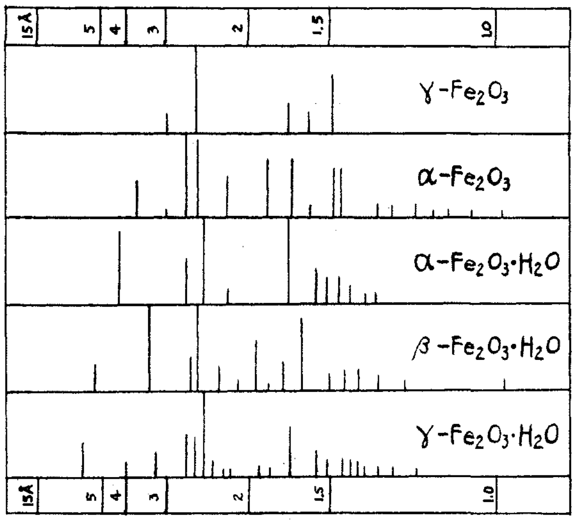

Fig. 1.—x-Ray diffraction patterns.

gram. As already mentioned, the brick-red precipitates listed in Table I were all found by x-ray analysis to be α-Fe_2O_3. Referring to Table III it will be noted that the diffraction data found experimentally agree with the calculated values assuming an orthorhombic structure having the lattice constants: $a_0 = 5.28$; $b_0 = 10.24$; $c_0 = 3.34$; $a:b:c = 0.516:1:0.326$. The density of the sample was found to be 3.14 when measured by the density bottle method, and 3.2 ± 0.1 when measured by flotation in a solution of potassium iodide and mercuric iodide. The density calculated from the x-ray data is 3.245 for a unit cell containing two molecules of $Fe_2O_3 \cdot H_2O$ or four molecules of FeOOH.

Dehydration Isobars.—Dehydration isobars for sample A containing appreciable chloride and samples E and F which are almost free from chloride are given in Figs. 2 and 3. Sample A was dehydrated in an apparatus already described[13] in which the water vapor pressure of the air passed over the sample was maintained at approximately zero. The color of the sample changed from yellow to red coincident with the sudden loss of water and hydrochloric acid at 150–184°. x-Ray analysis showed this red product to be α-Fe_2O_3. Since sample A contained considerable chloride it seemed advisable to repeat the dehydration experiment with samples containing but a small amount of chloride. Accordingly samples E and F were dehydrated in the same manner as sample A, except that the air passed over the sample was bubbled through distilled water kept at 25° in a thermostat. The results for the almost pure samples E and F indicate that the preparation is a definite hydrous monohydrate.

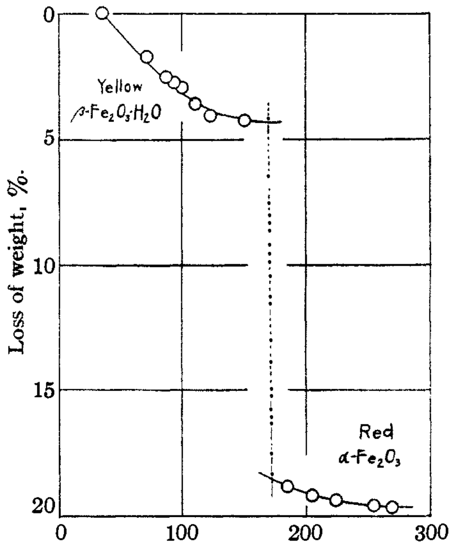

Fig. 2.—Dehydration isobar for sample A.

The dehydration of F was followed by means of x-ray diffraction patterns taken at various temperatures. At temperatures up to 100–125° the pattern, which was that of the monohydrate, remained constant. Above this range the diffraction lines became gradually weaker until at 150° some of them were barely discernible. The anhydrous oxide formed by the dehydration is too finely crystalline at this temperature to give a pattern; but at 165°, the strongest lines of both the monohydrate and of α-Fe_2O_3 were present. At 200°, the pattern contained only the lines of α-Fe_2O_3.

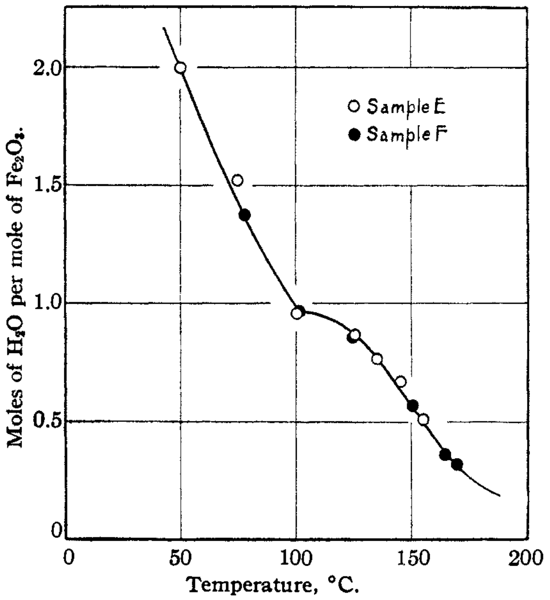

Fig. 3.—Dehydration isobar for samples E and F.

Discussion of Results

The slow hydrolysis of solutions of ferric chloride yields a yellow hydrous precipitate the chloride content of which varies with the exact conditions of formation and the subsequent treatment. Samples were prepared in which the ratio Fe : Cl was 45; a higher ratio could have been obtained if there were any point in doing so. Samples of the yellowish precipitate give identical x-ray diffraction patterns irrespective of the chloride content. This indicates that the precipitate is a ferric oxide with more or less adsorbed chloride and not a basic ferric salt. Dehydration isobars for the hydrous precipitate show a gradual

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(13) Weiser and Milligan, *J. Phys. Chem.*, **38**, 513 (1934).

loss of adsorbed water followed by an abrupt loss of chemically combined water corresponding to one mole per mole of Fe_2O_3. Since the particular structure has been obtained only by hydrolysis of ferric chloride,[14] it would appear that the adsorbed chloride stabilizes the crystal lattice. This is supported by the observation that a preparation containing appreciable adsorbed chloride starts to lose its hydrate water at a temperature 50° higher than does a relatively pure sample. The experimentally determined x-ray diffraction data agree with those calculated on the assumption that the crystals are orthorhombic and have the following lattice constants: a_0 = 5.28 Å.; b_0 = 10.24 Å.; c_0 = 3.34 Å. The density of the compound corresponds to the density calculated from the x-ray data on the assumption that the unit cell contains 2 molecules of $Fe_2O_3 \cdot H_2O$ or 4 molecules of FeOOH.

Since the two well-known monohydrates are α-$Fe_2O_3 \cdot H_2O$ and γ-$Fe_2O_3 \cdot H_2O$, the new monohydrate herein described has been termed β-$Fe_2O_3 \cdot H_2O$.

Summary

The slow hydrolysis of ferric chloride solutions that are not too dilute, yields a yellowish, hydrous precipitate which Böhm believed to be a basic chloride. Evidence obtained by x-ray analysis and isobaric dehydration indicates that this product is a third polymorph of ferric oxide monohydrate. The experimentally determined x-ray diffraction data agree with those calculated on the assumption that the crystals are orthorhombic and have the following lattice constants: a_0 = 5.28 Å.; b_0 = 10.24 Å.; c_0 = 3.34 Å. The compound has been designated β-$Fe_2O_3 \cdot H_2O$ to distinguish it from the well-known α- and γ-$Fe_2O_3 \cdot H_2O$.

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(14) Weiser and Milligan, *J. Phys. Chem.*, **39**, January (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. XLIII. I. The Atomic Weight of Europium. II. The Specific Gravity of Europium Chloride[1]

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The object of the work described in this paper was to determine the atomic weight of europium by using the chloride-to-silver ratio.

The atomic weight of europium in current use, 152.0,[2] is based on the work of Urbain and Lacombe,[3] and Jantsch[4] on the oxide-to-sulfate ratio. The disadvantages of the oxide-to-sulfate ratio have been discussed critically by Hopkins and Balke,[5] and Brauner and Švagr.[6] Since the atomic weight of europium has never been determined by the chloride-to-silver ratio, and since the difference between the atomic weights of europium and gadolinium is greater than the difference between the atomic weights of any other pair of rare earth elements, it was deemed advisable to redetermine the atomic weight of europium.

Purification of Europium Material

The original source of the europium material was Brazilian monazite. Two different quantities of the material were obtained from the Welsbach Company as the crude rare earth oxides. In both cases the cerium was removed by the permanganate-phosphate[7] method. The cerium free oxides were converted to the double magnesium nitrates and subjected to a series of fractional crystallizations. The samarium–europium–gadolinium[8] rich fractions at the more soluble end of the different series were combined in a new series.

After approximately 1000 fractionations, large amounts of bismuth magnesium nitrate were added for the dual purpose of (a) splitting[9] in between samarium and europium, and (b) increasing the bulk of material. After about 200 more fractionations, the europium–gadolinium fractions were converted to the simple nitrates, bismuth nitrate being used as the separating agent for the elimination of the samarium at the more soluble end of the series. After the removal of the major portion of the samarium by some 150 fractionations, the europium rich–gadolinium poor fractions were reconverted to the double magnesium

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(1) Summary of a thesis presented to the Graduate School of the University of Illinois by E. L. Meyers in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

(2) Report of the Committee on Atomic Weights of the International Union of Chemistry, THIS JOURNAL, **55**, 441 (1933).

(3) Urbain and Lacombe, *Compt. rend.*, **138**, 627 (1904).

(4) Jantsch, *ibid.*, **146**, 473 (1908).

(5) Hopkins and Balke, THIS JOURNAL, **38**, 2334 (1916).

(6) Brauner and Švagr, *Coll. Czecho. Chem. Communications*, **4**, 51 (1932).

(7) Neckers and Kremers, THIS JOURNAL, **50**, 955 (1928).

(8) All the fractionation of the samarium–europium–gadolinium material was carried out in this Laboratory by Drs. L. L. Quill and P. W. Selwood.

(9) This method of splitting in a separator element was probably first used by G. Urbain. He gives an excellent summary of his methods in *Chem. Rev.*, **1**, 155 (1924).