

## FERRIC CHLORIDES

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The classical investigation of Roozeboom and Schreinemakers<sup>2</sup> contains data for the solubility of ferric oxide in aqueous solutions of hydrochloric acid when the solution contains more than an equivalent amount of hydrochloric acid. The present investigation is an extension of this work at 25° C to cover the cases where there is present relatively more ferric oxide than acid. Roozeboom and Schreinemakers' results have been recalculated and included in Table I with the results obtained in the present investigation.

The hydrolysis of ferric chloride on the addition of water was noticed early by reason of the accompanying change in color and the subsequent precipitation of a dark brown body commonly identified as ferric hydroxide. It has been studied by a number of investigators, including Debray,<sup>3</sup> Krecke,<sup>4</sup> Fossereau,<sup>5</sup> Goodwin<sup>6</sup> and Spring.<sup>7</sup> Krecke found that the precipitated body contained no chlorine when left long in contact with solutions of ferric chloride, but gradually changed into the insoluble modification of ferric hydroxide first described by Pean de Saint Gilles.<sup>8</sup> He also found that the hydrolyzed iron was in the form of Graham's colloidal ferric hydroxide and measured the amount of the hydrolysis by precipitating the colloid with an electrolyte. The precipitated bodies were not oxychlorides, but ferric hydroxide.

Fossereau and Goodwin found that the hydrolysis took place slowly, as indicated by color change, and that the conductivity increased with the age of the solution.

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<sup>2</sup> Zeit. Phys. Chem., **15**, 588 (1894).

<sup>3</sup> Bull. Soc. Chim., Paris [2], **12**, 346 (1869).

<sup>4</sup> Jour. prakt. Chem. [2] **3**, 286 (1871).

<sup>5</sup> Comptes rendus, **103**, 42 (1886).

<sup>6</sup> Zeit. phys. Chem., **21**, 1 (1896).

<sup>7</sup> Rec. Trav. Pays-Bas., **16**, 237 (1897).

<sup>8</sup> Jahresb., **1855**, 401.

Spring suggested that ferric chloride was dissociated into ferrous chloride and chlorine, supporting his views by the fact that potassium ferricyanide gives a precipitate with certain concentrations of ferric chloride and that chlorine is observed to escape from concentrated solutions of ferric chloride.

Rousseau<sup>1</sup> found that by heating a concentrated solution of ferric chloride in sealed tubes, crystalline precipitates even obtained, containing different ratios of  $\text{Fe}_2\text{O}_3$  to  $\text{FeCl}_3$ , depending upon the temperature. The higher the temperature the less was the chloride present in the solid. By continued boiling in water, the chloride was gradually but completely removed, yielding crystalline ferric hydrates. The evidence recorded indicates the formation at higher temperatures of definite hydrated and anhydrous oxychlorides, but is not sufficient to negative the possibility that these supposed compounds actually belong to a series of solid solutions.

For the present work, aqueous solutions of varying concentrations of ferric chloride were treated with an excess of

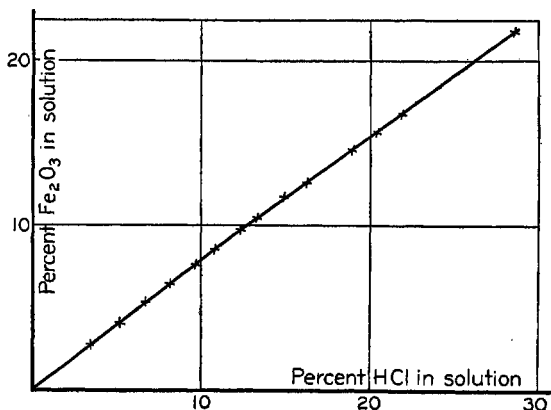


Fig. 1

freshly precipitated ferric hydroxide and shaken at a constant temperature of  $25^\circ\text{C}$  for three months, when the specific

<sup>1</sup> Comptes rendus, 110, 1032 (1890); 111, 542 (1891).

gravities of the solutions had become constant. The concentrations of the solutions were then determined, the data obtained being given in Table I, and charted in Fig. 1. It will be seen that the curve approximates a straight line, the deviation being slight, but real. It further appears that at 25° C solutions of ferric chloride have a less solvent effect on ferric hydroxide than has ferric sulphate.<sup>1</sup>

TABLE I

Complete isotherm for the system, ferric oxide, hydrochloric acid and water at 25° C.

Sp. gr. $\frac{25^\circ}{25^\circ}$	Percent $\text{Fe}_2\text{O}_3$	Percent HCl	Solid phase
—	34.61	59.88	$\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$
—	33.27	60.23	$\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$
—	32.78	54.71	$\text{FeCl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O} + \text{FeCl}_3$
—	31.95	58.20	$\text{FeCl}_3 + \text{FeCl}_3 \cdot 2\text{H}_2\text{O}$
—	34.42	59.12	$\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$
—	35.22	59.28	$\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$
—	34.07	55.71	$\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$
—	34.21	55.47	$\text{FeCl}_3 \cdot 2\text{H}_2\text{O} + \text{FeCl}_3 \cdot 2.5\text{H}_2\text{O}$
—	34.44	51.11	$\text{FeCl}_3 \cdot 2.5\text{H}_2\text{O} + \text{FeCl}_3 \cdot 3.5\text{H}_2\text{O}$
—	33.04	46.72	$\text{FeCl}_3 \cdot 3.5\text{H}_2\text{O} + \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
—	24.42	33.40	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
I. 485	21.84	29.33	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{Fe}_2\text{O}_3 \cdot x\text{HCl} \cdot \text{H}_2\text{O}$
I. 349	16.82	22.55	$\text{Fe}_2\text{O}_3 \cdot x\text{HCl} \cdot \text{H}_2\text{O}$
I. 321	15.83	21.10	"
I. 284	14.62	19.53	"
I. 242	12.59	16.61	"
I. 220	11.76	15.28	"
I. 195	10.56	13.76	"
I. 192	9.84	12.67	"
I. 158	8.60	11.24	"
I. 137	7.64	9.91	"
I. 115	6.47	8.39	"
I. 093	5.25	6.80	"
I. 070	4.04	5.36	"
I. 047	2.85	3.66	"

The compositions of some of the ferric chloride solutions with the compositions of their residues with adhering mother-

<sup>1</sup> Jour. Phys. Chem., 11, 641 (1907).

liquor are given in Table II and plotted on the triangular diagram of Fig. 2.

TABLE II

Composition of ferric chloride solutions with the corresponding solid residues and adhering mother liquor

Solutions		Residues	
Percent $\text{Fe}_2\text{O}_3$	Percent HCl	Percent $\text{Fe}_2\text{O}_3$	Percent HCl
2.85	3.66	14.67	3.69
5.25	6.80	28.31	5.97
7.64	9.91	31.62	8.33
9.84	12.67	26.41	11.01
10.56	13.76	21.13	12.31
12.59	16.61	24.51	14.52
14.62	19.53	30.28	15.61
16.82	23.22	29.02	18.20
21.84	30.20	30.40	22.45

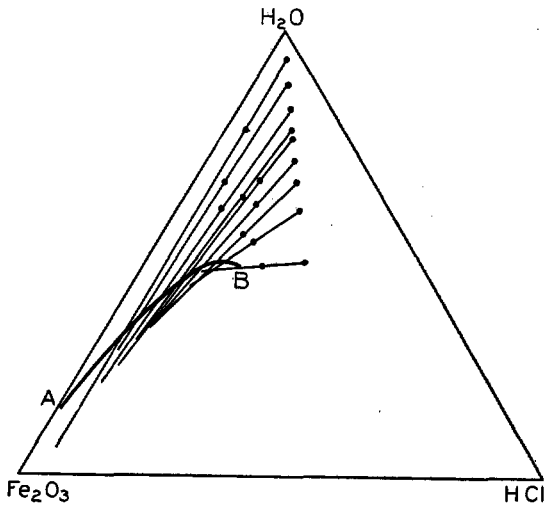


Fig. 2

By inspection of Fig. 2 it is apparent that the solid phase is of varying composition. If the lines were taken sufficiently near to each other the composition of the solid phases would

be shown by the envelope of their intersections, as indicated by the line AB.

From the data which has been obtained in this investigation of the system, ferric oxide, hydrochloric acid and water, it follows that at 25° C no definite basic chloride is formed, but that the stable solid phase is one of a series of solid solutions containing ferric oxide, hydrochloric acid and water.

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