500° but much faster at 690°. Under the microscope, the cupric oxide layer formed at 500° appeared much smoother than layers formed at higher temperatures.

The oxidation rates of other metals studied were not influenced by activating the oxygen. There is some indication that the rate of oxidation of molybdenum at 690° is somewhat retarded by activated oxygen.

It was not possible to correlate, in a quantitative way, the effects caused by activated oxygen with the concentration of free oxygen atoms. Probably the relation between free atom concentration in the gas phase and in the adsorbed layer on the surface of the oxide scale is quite complex.

From (1) measurements of the resistance of copper specimens at experimental temperatures in ordinary and in activated oxygen, (2) theoretical calculations which cannot be presented here because of space limitations, and (3) the fact that activated oxygen was found to accelerate as well as to retard the rate of oxidation, it follows that the effects observed in the oxidation of copper in activated oxygen are not due merely to the thermal effects of the recombination of oxygen atoms on the surface of the oxide scale.

Acknowledgment.—The author would like to express his appreciation to Dr. M. Kilpatrick, Dr. H. J. McDonald and Dr. D. D. Cubicciotti for encouragement and advice received during the course of this work, and to Dr. J. Whitney for help in the interpretation of the X-ray patterns.

Summary

The oxidation of copper, and several other metals, in ordinary and in activated oxygen are compared. Only in the case of copper are reproducible differences caused by the presence of an excess of free oxygen atoms in oxygen. Cases in which the monatomic oxygen accelerates, retards or does not influence the rate of oxidation are described. The conditions for the appearance of cupric oxide in the scale are outlined and an explanation of some types of complex oxidation curves is attempted.

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[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 1433]

The Distribution of Ferric Iron between Hydrochloric Acid and Isopropyl Ether Solutions. I. The Compound Extracted and the Extraction at Constant Acid Concentration

By Rollie J. Myers, David E. Metzler and Ernest H. Swift

Introduction

This series of papers presents the results of a continuation of the experimental work which has been in progress in this Laboratory on the distribution of certain inorganic compounds between immiscible liquid phases.

Dodson, Forney and Swift[1] have demonstrated that isopropyl ether could be used for the quantitative extraction of ferric iron from hydrochloric acid solutions; that the distribution of the iron was greatly dependent upon the acid concentration; and that, within certain limits, extraction was increased by an increase in acid concentration. They also observed that at a constant acid concentration the per cent. of iron extracted decreased when the total amount of iron present was decreased and that under certain conditions two ether phases were formed. This investigation was undertaken to examine the distribution process more closely, and especially to study these last two phenomena. During the preparation of these articles for publication a similar study was published.[2] Although the general experimental results are similar, our interpretation in some cases is different. Attention will be called to these differences in the subsequent articles.

Experimental Procedures

Distribution Procedure.—The aqueous hydrochloric acid-iron solutions were prepared in 25-ml. volumetric flasks. The contents of a flask was transferred to a 50-ml. ground-glass stoppered mixing cylinder and 25 ml. of ether was added. These cylinders were then shaken vigorously and placed in a thermostat regulated at 25.0 ± 0.02°. The cylinders were shaken vigorously for one minute at fifteen-minute intervals during one hour, then were shaken twice in ten minutes, and allowed to settle for at least five minutes, usually longer, before samples were removed.

The samples were removed from both layers with pipets, experiments having shown that the ether drainage did not introduce a significant error. For the analysis of iron in the ether layer the ether was removed by evaporation, or the iron was extracted by shaking the ether with several portions of water.

Analysis for Iron.—For quantities of iron greater than 0.5 millimole the iodometric procedure described by Swift[3] was used. For quantities less than 0.5 millimole and greater than 0.01 millimole this procedure was modified by bringing a 20-ml. portion of solution containing 24–48 millimoles of hydrochloric acid to a boil, flushing out the air with carbon dioxide, then stoppering the flask. The flask was at least twice more flushed with carbon dioxide while cooling. When cool, 3 g. of potassium iodide was added to the sample and the solution allowed to stand for one minute. Then 100 ml. of water was added and the solution was titrated with 0.01 *VF* (volume formal) sodium thiosulfate to

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[1] R. W. Dodson, G. J. Forney and E. H. Swift, This Journal, **58**, 2573 (1936).

[2] N. H. Nachtrieb and J. G. Conway, *ibid.*, **70**, 3547 (1948), and N. H. Nachtrieb and R. E. Fryxell, *ibid.*, **70**, 3552 (1948).

[3] E. H. Swift, *ibid.*, **53**, 2682 (1929).

a starch end-point. This method was found to give results accurate to one part per hundred.

For quantities of iron less than 1.6 micromoles and greater than 0.28 micromole a thiocyanate colorimetric method utilizing a Klett–Summerson photoelectric colorimeter and 10-ml. tubes was used. In order to minimize the error due to fading (about 1% per minute) the colorimeter readings were taken 1.5 minutes after the thiocyanate was added to the sample. One ml. of 3 *VF* potassium thiocyanate and enough hydrochloric acid to give a total acid content equivalent to 2 ml. of 6 *VF* acid per 11 ml. were taken. Over the range used, the method gave an excellent linear calibration curve.

For determining even smaller quantities of iron, the ultraviolet light absorption of the ether and aqueous layers was measured. A Beckman model DU spectrophotometer was employed and readings were taken at wave lengths of 364, 340, 316 and 287 mμ. With both layers a sample of the identical solvent without iron was used as a blank. Extinction coefficients were calculated by analysis of prepared solutions or by comparison with the colorimetric method. In Table I the extinction coefficients used for the ether layer are given.

TABLE I

THE ETHEREAL IRON EXTINCTION COEFFICIENTS

These values were obtained by comparison with the colorimetric method. There were six determinations at each wave length with an average deviation of 1.5%.

Wave length, mμ	364	340	316	287
Type	Max.	Min.	Max.	Min.
Extinction coeff., l./mole-cm. $\times 10^{-3}$ ($\log_{10}$)	6.96	3.80	6.34	3.70

Analysis for Acid.—After some experience it was realized that the dependence of the equilibrium upon the acid concentration was such that to warrant iron determinations accurate to within 1% the acid concentration would have to be known to 0.1%. Since the iron carries into the ether both acid and water it was necessary that the acidity of each individual distribution be determined. This was done by means of a modified Volhard chloride procedure.

Samples of the aqueous layers containing a little less than 10 milliequivalents of chloride were taken by weight. After the sample was diluted with 100 ml. of water, 50.00 ml. of 0.2 *VF* silver nitrate was added, the mixture heated until precipitate coagulated, filtered, and the precipitate washed with dilute nitric acid. When the filtrate was cool, ferric nitrate indicator was added, and it was titrated with 0.1 *VF* potassium thiocyanate, use being made of the ferric thiocyanate color for determining the end-point. The number of equivalents of thiocyanate required for the back-titration was usually less than 5% of the number of equivalents of chloride.

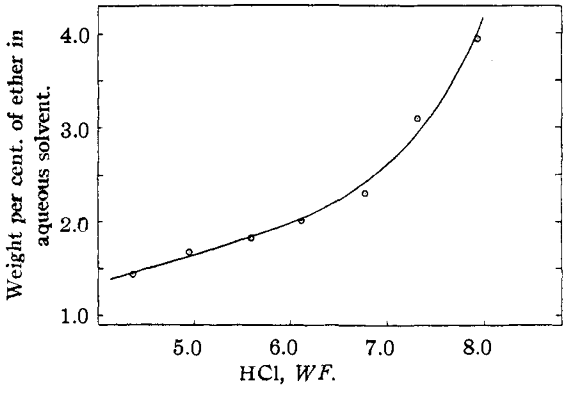

Fig. 1.—Solubility of isopropyl ether in aqueous hydrochloric acid solutions. The per cent. of isopropyl ether in the aqueous solvent (water and ether) is given as a function of the aqueous acid concentration. The values were determined by chloride analysis of the aqueous layer, corrections being made for the water and acid which passed into the ether layer.

The average deviation of these determinations was less than 5 parts per 10,000. The silver nitrate solution was standardized against samples of recrystallized potassium chloride.

The acid concentrations of the samples were calculated by subtracting three times the iron concentration from the chloride value. Since the hydrochloric acid concentration was in most cases large relative to that of the iron, the uncertainty in the chloride concentration caused by species such as $FeCl_2^+$ was usually small. The acidities will be expressed exactly as formula weights of hydrogen chloride per kilogram of solvent (*WF*) or approximately as formula weights per liter of solution (*VF*).

The nature of the aqueous layer varies with the acid concentration according to the solubility curve given for isopropyl ether in hydrochloric acid shown in Fig. 1. These values were determined by analyzing the hydrochloric acid solutions for chloride before and after equilibration with ether, corrections being made for the water and acid which passed into the ether layer. The equilibration was done for two hours at 25°.

Determination of the Formula of the Iron Compound in the Ether Layer.—Both the chloride and hydrogen associated with the extracted iron complex were determined by the methods used by Axelrod and Swift.[4] The hydrochloric acid dissolved in the ether layer of a blank distribution without iron was determined, and this quantity was subtracted from the total amount of acid found when iron was present.

The Zerewitinoff (Grignard) gasometric method for the determination of the water coördinated with the iron in the ether layer was tried. It was found, however, that methylmagnesium iodide and several higher Grignards reacted with the ferric iron, apparently causing reduction of the iron with the occasional slow production of a gas. This gas would generally not be expected to consist of only the basic hydrocarbon.[5] The method, therefore, was not used. It is possible that the amount of associated water reported by Nachtrieb and Conway[3] is in error for this reason.

The Karl Fischer method was employed, use being made of the directions of Wernimont and Hopkinson[6] and their deadstop end-point. It was found that again ferric iron was reduced by the reagent. However, this reaction appeared to be a stoichiometric reduction to the ferrous state. To test this hypothesis, anhydrous ferric chloride was prepared by the action of chlorine upon iron. Samples of this ferric chloride were added to methanol containing some hydrogen chloride and a known quantity of water. The resulting solution was then titrated with the Karl Fischer reagent in the usual manner. The results of two such experiments, collected in Table II, show that there is a simple relationship between the amount of ferric iron present and the effective water titer. Since in the Karl Fischer reaction ap-

TABLE II

THE REACTION BETWEEN FERRIC CHLORIDE, WATER AND THE KARL FISCHER REAGENT

	Expt. *A*	*B*
No. of millieq. of K.-F. reagent used	0.996	1.201
One-half the no. of formula wts. $\times 10^3$ of $FeCl_3$ added	0.346	0.130
Their sum	1.342	1.331
No. formula wts. $\times 10^3$ of water added	1.328	1.303
Percentage difference	1.0	2.1

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(4) J. Axelrod and E. H. Swift, THIS JOURNAL, **62**, 33 (1940).

(5) M. S. Kharasch and M. Kleiman, *ibid.*, **65**, 491 (1943).

(6) G. Wernimont and F. J. Hopkinson, *Anal. Chem.*, **15**, 272 (1943).

parently one formula weight of I_2 is used per formula weight of H_2O, it would appear that one formula weight of ferric iron caused the effective production of one-half formula weight of I_2. To test the precision of the titration when iron is present, the order of the titration and of the addition of the sample were varied; however, the titer was not found to change.

By separate experiment the solubility of water in the ether was determined for varying acid concentrations.

The results are shown in Fig. 2. This quantity of water was subtracted from the total water titer in order to calculate the amount of water coördinated with the iron. The average deviation of the water determinations was less than 1%.

Reagents.—The hydrochloric acid and ferric chloride were of "Reagent" grade. The stock solutions of ferric chloride were kept at least 0.02 *VF* in hydrochloric acid to minimize hydrolysis.

Because of its use in ultraviolet absorption spectra measurements and because of the small quantities of iron used, it was deemed necessary that the ether should be free from impurities, especially peroxides. It was also advantageous to use a single sample of ether for the entire experimental period. It was found that sodium purified isopropyl ether could be kept peroxide-free for several months by the addition of 10^{-5} formula weight/l. of hydroquinone or catechol.

An experiment was conducted to test this procedure: 40-ml. portions of sodium-purified peroxide-free isopropyl ether were distilled into 60-ml. clear glass bottles containing different quantities of inhibitor, and these bottles were then stored under different conditions. The ether was tested for peroxide by shaking a sample with a titanic chloride-hydrochloric acid solution. The test was considered positive when the resulting color was the same as or greater than that given when hydrogen peroxide sufficient to make the solution 10^{-4} *VF* had been added. The results of the tests are shown in Table III.

TABLE III

THE EFFECT OF STORAGE AND INHIBITOR UPON PEROXIDE FORMATION IN ISOPROPYL ETHER

Inhibitor	Quantity f. wts./l.	Storage	Time for a positive test
None	..	Dark	1 day
Hydroquinone	10^{-6}	Dark	4 days
Hydroquinone	10^{-5}	Diffuse light	3 weeks
Hydroquinone	10^{-5}	Dark	>9 months
Hydroquinone	10^{-4}	Dark	>9 months
Catechol	10^{-6}	Dark	3 days
Catechol	10^{-5}	Dark	>9 months
Catechol	10^{-4}	Dark	>9 months

The sample of ether used for all of the experiments described was purified by treatment with 10–20 g. of sodium per liter. It was then distilled through an efficient column into a quantity of catechol sufficient to make the concentration 10^{-5} *VF*. The fraction used distilled between 67.8 and 68.2° (cor.) and stayed peroxide-free over the entire experimental period.

Since catechol has strong light absorption near 270 mμ, for some of the spectrophotometric and distributive work the catechol was removed by distillation. Distributions with and without catechol originally present in the ether gave the same results even when the total iron content was very small. It was found that low colorimetric readings were obtained if ether layers containing catechol and less than 0.3 millimole/l. of iron were evaporated to dryness. This error was eliminated by evaporating the ether samples after adding an equal quantity of 1 *VF* hydrochloric acid. The ether purified as stated and with the catechol removed was found to have strong light absorption below 260 mμ. When this ether was shaken with concentrated hydrochloric acid, spectrophotometric readings could be taken down to 230 mμ. However, the absorption spectrum indicated that some impurities were still present.

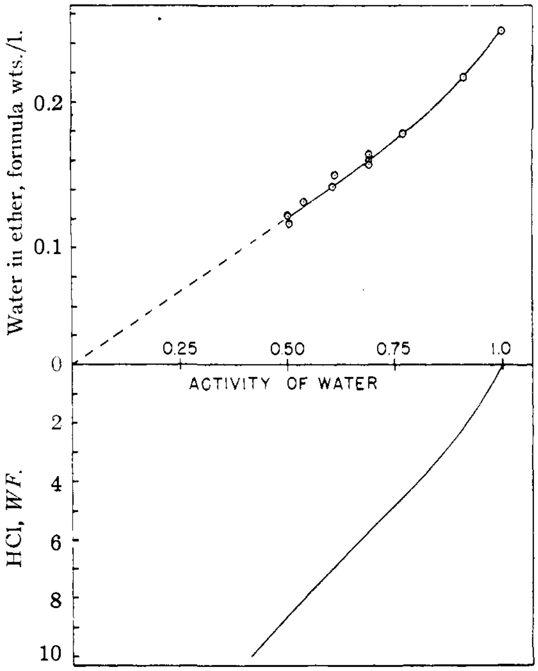

Fig. 2.—The distribution of water between isopropyl ether and aqueous hydrochloric acid. By the use of a dual plot the water dissolved in the ether is shown both as a function of the activity of water and of the acid concentration. The activity data are those of Randall and Young.[7]

Experimental Results

The Compound Extracted.—It has been shown[8,9] that when ethyl ether is used the compound extracted is $FeCl_3\cdot nHCl$ where *n* is unity at low acid concentrations and becomes greater than unity when the acid concentration is increased. When β,β'-dichloroethyl ether is used the formula of the iron complex is $FeCl_3\cdot HCl$[4] even when extracted from 8 *VF* hydrochloric acid.

An extensive investigation of the number of hydrogen chloride molecules in the extracted complex was not made. However, some experiments were performed, and these are collected in Table IV. Nachtrieb and Conway[2] have shown that when the initial acid concentration is less than 7 *VF* the compound extracted is $FeCl_3\cdot HCl$. When the initial concentration is greater than 7 *VF*, however, there seems to be more than one hydrogen chloride associated with each iron even when a correction is made for the dissolved hydrogen chloride. As will be shown in a subsequent paper, the visible and ultraviolet absorption spectra do not change in form when this higher acid association takes place. It is conceivable that this additional acid is associated with the coördinated water or ether and not directly with the iron.

The water coördinated with the ethereal iron was determined by titration with the Karl Fischer reagent as described above. The variation of this associated water with the acid concentration and with the ethereal iron concentration is shown in Fig. 3. Since the number of water molecules coördinated with each iron varies with the acid concentration over the concentration range studied, more than one hydrate must exist in the ether layer. Also, since the number of water molecules varies with the iron concentration at a constant acid concentration it is indicated that

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(7) M. Randall and L. E. Young, THIS JOURNAL, **50**, 989 (1928).

(8) S. Kato and R. Ishii, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **36**, 82 (1939).

(9) Nekrosov and Ousyankina, *J. Gen. Chem.* (*USSR*), **11**, No. 8573 (1941), see *Chem. Abs.*, **35**, 7266 (1941).

TABLE IV

THE COÖRDINATION OF CHLORIDE AND HYDROGEN IN THE EXTRACTED COMPLEX

Series A[a]: aqueous layer, 3 *VF* HCl and 2 *VF* NaCl; blank correction for acid in ether, 1.3 × 10^{-3} *VF*.

Ethereal iron f. wts./l. × 10^3	Chloride/iron	Hydrogen/iron
1.52	4.08	1.11
2.10	3.87	0.85
7.37	4.00	0.91
7.69	4.16	0.94

Series B[b]: aqueous layer, 7.5 *VF* HCl. In these extractions two ether phases were present; blank correction for acid in ether, 2.46 × 10^{-2} *VF*.

Ethereal iron f. wts./l.		Chloride/iron		Hydrogen/iron	
Light layer	Heavy layer	Light layer	Heavy layer	Light layer	Heavy layer
0.102	0.334	4.22	4.30	1.29	1.25
.105	.324	4.20	4.30	1.23	1.36
.104	.332	4.21	4.30	1.19	1.23
.111	.392	4.34	4.39	1.17	1.27

[a] Experimental work by Joseph Green, John Gryder and David Metzler. [b] Experimental work by Richard Dodson.

there is more than one iron atom in some of the hydrates, or, stated otherwise, that there is some type of polymerization of the ethereal iron. It should be noted that the decrease in analyzed water shown in Fig. 3 for 5.6 *WF* acid is greater than the solubility of water in ether with no iron present.

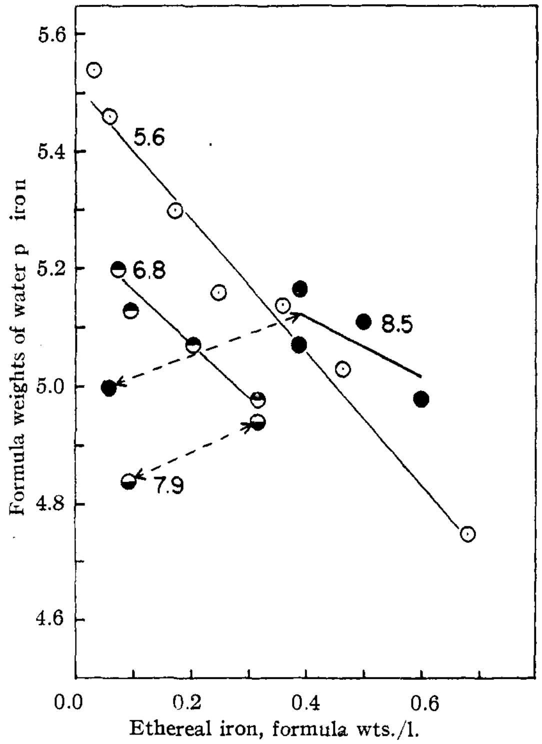

Fig. 3.—The coördination of water in the extracted complex: ⊙, extraction from 5.60 *WF* acid; ◓, extraction from 6.77 *WF* acid; ⊖, extraction from 7.93 WF. acid; ●, extraction from 8.46 *WF* acid. Dotted arrows join the points representing the region over which two ether phases are present.

At the two highest acidities studied, over a certain range of iron concentration, there were two ether phases present. In Fig. 3, the region over which there were two ether phases is indicated by the dotted lines. A more detailed discussion of this two-ether-phase region will be given in the following paper.

Extraction at a Constant Acid Concentration.—Dodson, Forney and Swift[1] found that the percentage of extraction decreased when the total amount of iron present was decreased while the acid concentration was held approximately fixed. Qualitatively, this can be explained by assuming that the iron polymerizes in the ether layer. If this effect is to be quantitatively studied, the acid concentration must be carefully controlled, because of the great dependence of the extraction upon acidity, and the total amount of iron in the aqueous layer must be sufficiently small so that its effect upon ionic strength can be neglected. As a compromise between this latter effect and that of ease of analysis, 5 *VF*

TABLE V

THE DISTRIBUTION WITH A FIXED ACID CONCENTRATION

The acid concentration was individually determined for every distribution except the first five. Corrections were made for deviations from the mean value of 5.602 *WF* by computing an "adjusted" aqueous iron concentration as described in Part II, under "Variation of the Distribution Constant with Acid Concentration."

Ethereal iron *Q*, f. wts./l. × 10^3	Aqueous iron "adjusted" *F*, f. wts./l. × 10^3	Distribution ratio, *Q/F*
0.0136	0.0405	0.336
.0189	.0586	.322
.0243	.0734	.318
.0427	.132	.323
.0758	.234	.324
.0807	.255	.316
.128	.406	.315
.149	.473	.316
.255	.804	.317
.398	1.20_9	.329
.649	1.91_2	.339
.936	2.78	.337
2.28	6.26	.365
2.98	7.54	.395
3.78	9.01	.419
5.36	11.71	.458
7.44	13.98	.532
8.93	16.02	.557
11.09	17.31	.641
11.10	17.32	.641
13.51	18.42	.733
16.16	20.1_0	.804
17.07	20.3_0	.842
18.58	20.9_0	.889
24.5_5	22.95	1.07_0
27.5_4	23.55	1.16_8
31.6	24.5	1.30
41.0	26.0	1.58
49.0	26.0	1.89
55.0	26.2	2.11
63.3	27.0	2.35
75.6	27.2	2.78
137.0	28.7	4.77
227.2	29.4	7.72
341.4	32.0	10.6_6
476.2	35.5	13.4_0
672.8	54.1	12.4_5

(5.6 *WF*) was selected as the acid concentration at which to make a detailed study.

By the use of iodometric, colorimetric and spectrophotometric methods of iron analysis, and a chloride analysis for the acid, we obtained the data in Table V. Corrections were made for the deviations of the actual acid concentration from 5.602 *WF* (they were less than 1%) as described in Part II of this series by making use of knowledge of the variation of the extraction with acidity and computing an "adjusted" aqueous iron concentration. These data are also presented in a logarithmic plot, Fig. 4. Our results are very similar to those obtained by Nachtrieb and Fryxell.[2] Their experiments were done at 20°, and they did not determine the equilibrium acidities. Our data seem to be of higher precision.

It is apparent that at low iron concentrations the distribution ratio is approximately constant. As the iron concentration increases, however, the distribution ratio deviates quite sharply from constancy. At still higher iron concentrations the distribution ratio not only ceases to increase but actually decreases.

Nachtrieb and Fryxell,[2] relying upon an experiment in which ferric chloride and aluminum chloride mixtures were used, attribute this first increase in the distribution ratio to the effect of the increasing aqueous iron concentration upon its activity. At the acidity used in the experiment shown in Table V the increasing aqueous iron concentration probably has some effect upon the extraction; however, at one region the distribution ratio increases greatly while the aqueous iron concentration remains relatively constant. For example, according to their view, a 30% increase in the aqueous iron concentration near 0.025 *VF* is accompanied by an 800% increase in the aqueous iron activity. Such a large activity effect would not be expected in a solution so dilute in the substance in question. It is for this reason and others presented later that we take the view that the deviation of the extraction from ideality is due to polymerization of the ethereal iron.

Acknowledgments.—The authors are obligated to A. C. Custer, Richard Dodson, Joseph Green, and John Gryder, for data from unpublished experiments made at the California Institute of Technology. These data, some of which have been presented above, have allowed the authors to carry on a much more logical plan of research. The advice and assistance of Dr. Jurg Waser, and suggestions by Mr. David L. Douglas and Mr. Paul S. Farrington, have been very helpful. We are especially indebted to Dr. N. H. Nachtrieb for valuable suggestions made after reading the preliminary manuscript.

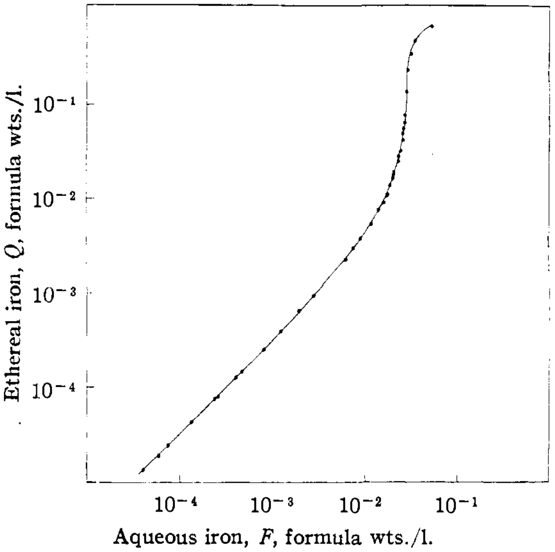

Fig. 4.—The distribution with a fixed acid concentration. The data in Table V are plotted logarithmically.

Summary

The formula of the iron complex extracted from aqueous hydrochloric acid-ferric chloride solutions by isopropyl ether has been established with respect to associated chloride, hydrogen, and water. The nature of the distribution of the ferric iron between the aqueous and ether layers at a constant acid concentration has been investigated. The dependence of the distribution ratio upon the aqueous iron concentration can be qualitatively explained in terms of polymerization of the ethereal iron. The variation of the number of associated water molecules with the variation of the ethereal iron concentration also indicates association of this iron.

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