

absorption spectrum quite unlike that of the ether-extracted complex. The absence of the 532, 618 and 685 millimicron bands in the spectrum of ferric chloride in 7.5 molar hydrochloric acid suggests that the complex does not exist in the aqueous phase to any appreciable extent. Table IV summarizes the extinction-concentration data obtained.

**Acknowledgment.**—This paper is based in part upon work performed under Contract No. W-7405-Eng-36 with the Manhattan Project at the Los Alamos Scientific Laboratory of the University of California.

### Summary

The empirical formula of the iron compound extracted from aqueous ferric chloride which does not exceed 8 molar in hydrochloric acid is  $\text{HFeCl}_4$ . For aqueous hydrochloric acid concentrations ex-

ceeding 8 molar the mole ratio of hydrogen chloride to ferric chloride exceeds 1:1. Determinations of water co-extracted with  $\text{HFeCl}_4$  by isopropyl ether indicate about ten moles of water per gram atom of iron. Data are presented showing the variation of the partition coefficient as a function of temperature, and a heat of extraction of  $-1970$  calories per mole is found for 0.9595 molar ferric chloride in 3.50 molar hydrochloric acid. The absorption spectra of the ether-extracted complex, anhydrous ferric chloride in isopropyl ether, aqueous ferric chloride, and a hydrochloric acid solution of ferric chloride are compared. The 532, 618 and 685 millimicron absorption bands of the ether-extracted complex conform to Beer's law. This is considered evidence for the existence of a single iron species in the ether phase over the concentration range 0.01 to 0.4 molar.

SANTA FE, NEW MEXICO

RECEIVED MAY 10, 1948

[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, THE UNIVERSITY OF CHICAGO]

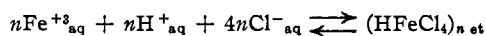
## The Extraction of Ferric Chloride by Isopropyl Ether. II

BY NORMAN H. NACHTRIEB AND ROBERT E. FRYXELL

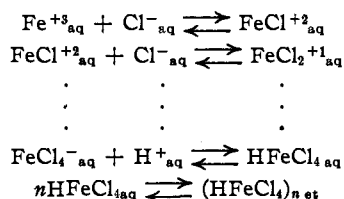
This second paper of the series,<sup>1</sup> adds experimental evidence to the observation of Dodson, Forney and Swift<sup>2</sup> that the distribution ratio of iron between isopropyl ether and aqueous hydrochloric acid varies with the total iron concentration. A complete explanation of the phenomenon is not yet possible, however; activity data for ferric chloride in concentrated hydrochloric acid solutions and for  $\text{HFeCl}_4$  in isopropyl ether must be obtained before equilibrium calculations which have any meaning may be made. Axelrod and Swift,<sup>3</sup> in discussing the anomalous extraction of ferric chloride by ethers cited unpublished work of Dodson, stating ". . . it seemed necessary to assume polymerization of the iron in the ether layer in order to explain the dependence of the distribution ratio upon the concentration of iron." Analyses of ethyl ether phases for iron and water by Kato and Ishii<sup>4</sup> and by Axelrod and Swift<sup>3</sup> (of  $\beta, \beta'$ -dichlorodiethyl ether) indicated a mole ratio  $(\text{H}_2\text{O})/(\text{Fe})$  of 4.5. Each group independently suggested the likelihood of a dimeric iron complex of the basis of this observation. The possibility of still higher even-numbered iron polymers (*e. g.*, a tetramer or a hexamer) or of mixtures of odd- or even-numbered iron polymers cannot, of course, be excluded. However, it is not possible to conclude that the water/iron ratio has any real significance as far as polymerization is concerned

unless it is shown that the water is an essential part of the extracted iron complex; the water may owe its existence in the ether phase to anomalous solubility effects induced by the presence of  $\text{HFeCl}_4$  in the ether. In this event, there is no reason why any integral ratio of water to iron concentrations should be expected.

It is clear that if polymerization of  $\text{HFeCl}_4$  in the ether phase be the cause of the failure of the simple Nernst distribution law some equation of the following type must describe the over-all reaction



Such an equation might be the sum of a series of equations of the sort



Certain of these equilibria would probably be shifted far "to the right" and justify simplification of the over-all picture. In any case, it may be simply shown for sequential equilibria of this type that the form of the distribution law on the assumption of a polymerized ethereal iron complex would be

$$(\text{Fe})_{n_{\text{et}}}/(\text{Fe})_{\text{aq}} = K_{(\text{H}^+),(\text{Cl}^-)} \text{const.} \quad (1)$$

under conditions of constant aqueous hydrogen and chloride ion activities. It is understood that the bracketed quantities must refer to activities if

(1) I. N. H. Nachtrieb and J. G. Conway, *THIS JOURNAL*, **70**, 3547 (1948).

(2) R. W. Dodson, G. J. Forney and E. H. Swift, *ibid.*, **58**, 2573 (1936).

(3) Axelrod and E. H. Swift, *ibid.*, **62**, 33 (1940).

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

$K$  is to be a true thermodynamic constant. Whatever the predominant species of aqueous ion containing iron be, its concentration will be proportional to the stoichiometric iron concentration, which is analytically determined. Equation 1 may be expressed in logarithmic form, as

$$\log (\text{Fe})_{\text{et}} = \log K + n \log (\text{Fe})_{\text{aq}} \quad (2)$$

from which it appears that the association number,  $n$ , would be the slope of a plot of the logarithm of the ethereal iron activity against the logarithm of the aqueous iron activity for extractions performed under conditions of constant aqueous hydrogen and chloride activity and of varying total iron concentration. In the following are discussed the experiments upon which one of us (N.H.N.) first concluded that a tetrameric ethereal iron complex was formed, and later experiments which have caused us to abandon this view as unproved.

### Experimental Procedure. A

The conditions of extraction and the methods of analysis employed in the first series of experiments were essentially those which have been previously described.<sup>1</sup> A series of extractions was performed at 25.0° in which the initial aqueous hydrochloric acid concentration was 3.6 molar throughout and the initial aqueous ferric chloride concentration varied from 0.0846 molar to 1.692 molar. The analyses of the aqueous and ethereal phases following extraction are given in Table I. A plot of log ethereal iron concentration against log aqueous iron concentration is given in Fig. 1. A second series of extractions was performed in which the initial ferric ion and hydrogen ion concentrations were 1.0016 and 5.00 molar, respectively, throughout and the initial aqueous chloride ion concentration varied from 0.50 to 4.00 molar. Ferric ammonium sulfate and nitric acid were the source of ferric and hydrogen ions; hydrochloric acid was added to provide the desired chloride ion concentration, and the concentration of nitric acid diminished in order to maintain constant initial aqueous hydrogen ion concentration. Table II summarizes the analyses performed on the aqueous and ethereal phases, and Fig. 2 shows a plot of log ethereal chloride concentration against log aqueous chloride concentration.

TABLE I

DISTRIBUTION OF FERRIC CHLORIDE BETWEEN AQUEOUS HYDROCHLORIC ACID AND ISOPROPYL ETHER

(HCl) <sub>i</sub>	(Fe) <sub>i</sub>	(Fe) <sub>et</sub>	(Fe) <sub>aq</sub>	(Cl <sup>-</sup> ) <sub>aq</sub>	(H <sup>+</sup> ) <sub>aq</sub>
3.594	1.692	0.963	0.5840	3.750	
3.594	0.846	.474	.3145	3.672	
3.594	.423	.0866	.301	3.613	3.602
3.594	.1692	.004277	.1496	3.536	3.546
3.594	.0846	.000338	.0772	3.506	3.644 <sup>a</sup>

<sup>a</sup> Over-titrated.

TABLE II

DISTRIBUTION OF FERRIC CHLORIDE BETWEEN AQUEOUS HYDROCHLORIC ACID AND ISOPROPYL ETHER

(Fe) <sub>i</sub>	(H <sup>+</sup> ) <sub>i</sub>	(Cl <sup>-</sup> ) <sub>i</sub>	(Cl <sup>-</sup> ) <sub>aq</sub>	(Cl <sup>-</sup> ) <sub>et</sub>
1.016	5.00	4.00	2.841	1.255
1.016	5.00	2.00	1.876	0.221
1.016	5.00	1.00	0.905	.02525
1.016	5.00	0.75	.807	.00895
1.016	5.00	.50	.545	.001294

### Discussion A

The log-log plot of Fig. 1 appears to be a straight line over the concentration range covered

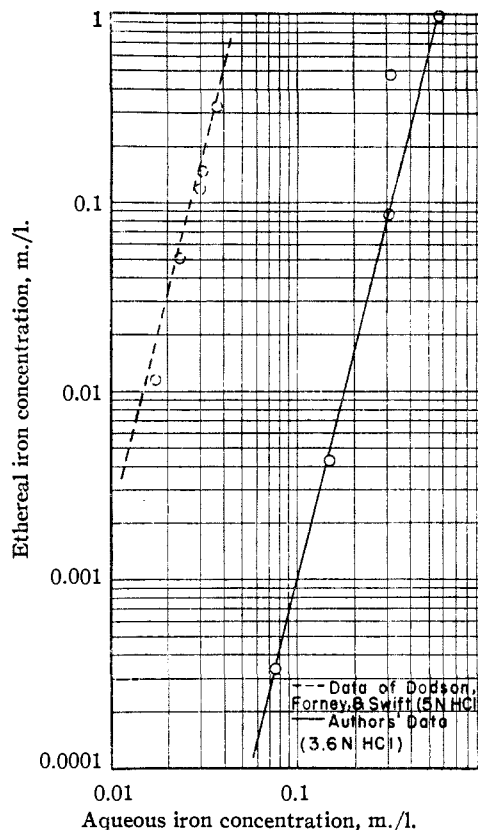


Fig. 1.—Variation of distribution with iron concentration for constant hydrochloric acid concentration.

and has a slope equal to 4.00. This was interpreted to indicate the formation of an ethereal iron complex containing four atoms of iron, although concentrations of the iron compounds were used instead of activities and notwithstanding the minor deviations from constancy which existed in the final aqueous hydrogen and chloride ion concentrations. The log-log plot of Fig. 2 is also a straight line with a slope equal to 4.08. This was again considered to be evidence for a tetrameric ethereal iron complex and to indicate the predominant species of iron associated with chloride in the aqueous phase to be  $\text{FeCl}_4^-$ , although again no activity coefficient data were available to permit the use of activities instead of concentrations in attempted equilibrium calculations. The authors were aware of the spectroscopic study of Rabinowitch and Stockmayer<sup>5</sup> on the association of ferric ions with chloride ions, but the equilibrium constants found by them were for solutions of about unit ionic strength and were not corrected for the deviations of concentrations from activities. These authors suggest that the data of Dodson, *et al.*, indicate the existence of a polymer in the ether phase. However, their observation: "This contradicts the results of molecular weight determinations of ferric chloride in organic solvents"

(5) E. Rabinowitch and W. H. Stockmayer, *THIS JOURNAL*, **64**, 335 (1942).

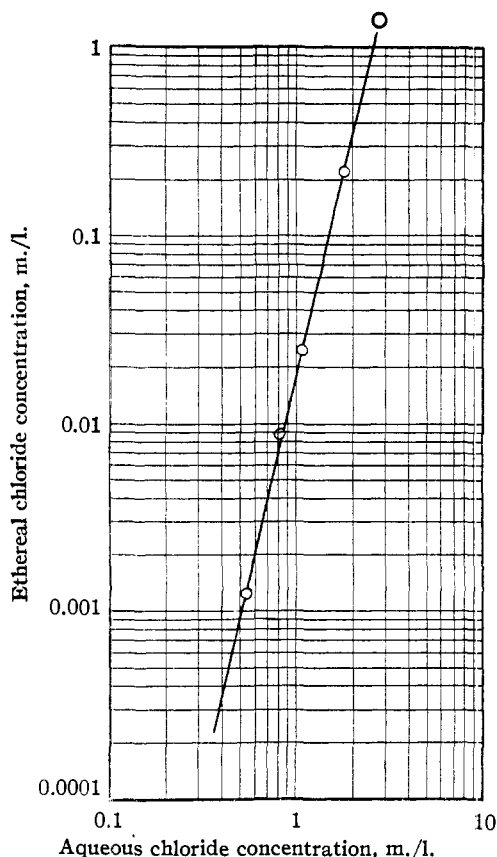


Fig. 2.—Variation of distribution with chloride concentration for constant iron and acid concentration.

is not valid, since it has been shown<sup>3,4</sup> that it is a compound of empirical formula,  $\text{HFeCl}_4$ , and not  $\text{FeCl}_3$ , which is ether-extracted.

The present authors' attempts to correlate the variation of the iron distribution coefficient with hydrochloric acid concentration by the use of Linhart's data for the activity of aqueous hydrochloric acid<sup>6</sup> on the assumption of an ethereal tetrameric iron complex were unsuccessful, and it was realized that the hypothesis was not a valid one.

A second series of experiments was undertaken in which an attempt was made to maintain essentially constant aqueous hydrogen and chloride ion concentrations and constant concentration of total trivalent cations. Aluminum chloride and ferric chloride stock solutions were mixed in such ratios as to keep their combined concentration fixed at 0.500 molar in 4.500 molar hydrochloric acid. Table III gives the analyses of the aqueous and ethereal phases for ferric ion, and Fig. 3 shows a plot of the ethereal iron concentration against the aqueous iron concentration. The curve appears to consist of two straight line portions, but it must be borne in mind that the final total tri-

(6) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 336.

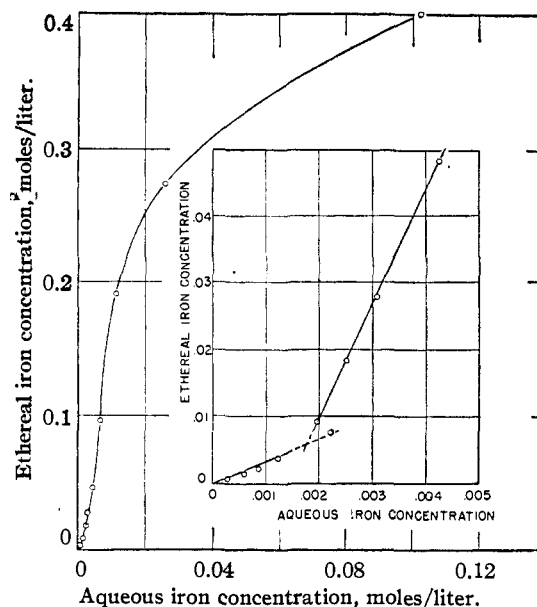


Fig. 3.—Variation of distribution with iron concentration for constant hydrochloric acid concentration; combined aluminum chloride plus ferric chloride concentration constant.

valent cation concentration in the aqueous phase is low by the concentration of iron which has been extracted into the ether. Correction for this effect would probably result in a parabola-like curve, replacing the two straight lines. The bending of the other curve at higher iron concentrations is due to a variety of causes, among which are: (1) decrease in the aqueous hydrochloric acid concentration, (2) decrease in the aqueous concentration of total trivalent cations due to removal of ferric chloride, and (3) the approach to saturation of  $\text{HFeCl}_4$  in isopropyl ether (see later). The effect of the aluminum chloride is seen to be to increase the efficiency of extraction of low concentrations of iron, although it does not quite succeed in making the distribution coefficient independent of the total iron concentration. Inasmuch as this non-extractable salt is capable of greatly increasing the efficiency of extraction, it seems unnecessary to attribute the effect of increased efficiency with rising concentrations of iron to polymerization.

We are now led to consider the interesting alternative to the hypothesis of polymerization of the ethereal iron complex that the cause of the anomalous extraction of ferric chloride (*i. e.*, its increased efficiency with increasing total iron concentration) is a self-salting out effect of ferric chloride. On this view the activity of ferric chloride in high concentration of aqueous hydrochloric acid increases much more rapidly than the concentration of ferric chloride. The effect of the aluminum chloride is considered to be a diverse ion effect, in which aluminum ion (aluminum chloride is not extracted by ether) increases the activ-

TABLE III  
EXTRACTION OF FERRIC CHLORIDE FROM SOLUTION CONTAINING ALUMINUM CHLORIDE ( $t = 20.0 \pm 0.1^\circ$ )

(HCl) <sub>1</sub>	(AlCl <sub>3</sub> ) <sub>1</sub>	(FeCl <sub>3</sub> ) <sub>1</sub>	(Fe) <sub>aq</sub>	(Fe) <sub>et</sub>	(H) <sub>et</sub> <sup>c</sup>	(Cl) <sub>et</sub> <sup>c</sup>	$\frac{(\text{Fe})_{\text{et}}}{(\text{Fe})_{\text{aq}}}$	Empirical <sup>d</sup> formula (in ether)
4.500	0.500	0.00000	0.000000 <sup>a</sup>	0.000000 <sup>a</sup>	....	....	...	.....
4.500	.499	.00100	.000359 <sup>a</sup>	.000717 <sup>a</sup>	....	....	2.00	.....
4.500	.498	.00200	.000577 <sup>a</sup>	.001424 <sup>a</sup>	....	....	2.47	.....
4.500	.497	.00300	.000869 <sup>a</sup>	.002096 <sup>a</sup>	....	....	2.41	.....
4.500	.495	.00500	.001227 <sup>a</sup>	.003727 <sup>a</sup>	....	....	3.04	.....
4.500	.490	.0100	.002235 <sup>a</sup>	.00770 <sup>a</sup>	....	....	3.45	.....
4.500	.490	.0100	.00195 <sup>b</sup>	.00902 <sup>a</sup>	0.0095	0.0435	4.62	FeCl <sub>3</sub> ·1.05HCl
				.00849 <sup>b</sup>			4.35	
4.500	.480	.0200	.00254 <sup>b</sup>	.0182 <sup>a</sup>	.0189	.0763	7.16	FeCl <sub>3</sub> ·1.04HCl
				.0182 <sup>b</sup>				
4.500	.470	.0300	.00308 <sup>b</sup>	.0278 <sup>b</sup>	.0296	.1147	9.03	FeCl <sub>3</sub> ·1.06HCl
4.500	.450	.0500	.00425 <sup>b</sup>	.0485 <sup>b</sup>	.0464	.1953	11.4	FeCl <sub>3</sub> ·0.95HCl
4.500	.400	.1000	.00652 <sup>b</sup>	.0971 <sup>b</sup>	.0929	.3851	14.9	FeCl <sub>3</sub> ·0.95HCl
4.500	.300	.2000	.0112 <sup>b</sup>	.1932 <sup>b</sup>	.1706	.7618	17.2	FeCl <sub>3</sub> ·0.89HCl
4.500	.200	.3000	.02615 <sup>b</sup>	.2740 <sup>b</sup>	.2544	....	10.5	.....
4.500	.000	.500	.1019 <sup>b</sup>	.403 <sup>b</sup>	.3601	1.587	3.92	FeCl <sub>3</sub> ·0.90HCl
				.3991 <sup>b</sup>				

<sup>a</sup> Spectrophotometric, using *o*-phenanthroline. <sup>b</sup> Reduction by Jones reductor, followed by permanganate titration with preventive solution. <sup>c</sup> Corrected for solubility of hydrochloric acid in isopropyl ether (0.0056 molar). <sup>d</sup> Calculated from iron and hydrogen ion determinations.

ity of ferric ion in much the same way as ferric ion promotes its own activity. To establish this hypothesis, further experiments of this type must be carried out, using other polyvalent and monovalent cations.

Believing in the essential correctness of this hypothesis we were then led to predict that for ferric chloride solutions of sufficiently low concentration (such that concentrations may be considered equivalent to activities) a condition of normal partition of iron between the two phases should prevail. The solvent may be considered to consist of hydrochloric acid and water, and if its composition remain invariant will behave as a *pure* solvent. Thus, for any particular concentration of aqueous hydrochloric acid, this mixed solvent will behave as a pure solvent as long as its composition remains constant. If now the concentration of aqueous ferric chloride be diminished, an approach to the laws of the infinitely dilute solution should be realized. Each different concentration of aqueous hydrochloric acid will comprise a new "solvent," of course, with the consequence that the standard reference states of the solute will be different. We may define the standard state for the aqueous ferric chloride to be an infinitely dilute solution of ferric chloride in hydrochloric acid of stated concentration. To facilitate the analysis of the phases of very low iron concentration it was convenient to use radioactive iron in the manner described as follows:

#### Experimental Procedure B

0.3940 gram of iron which had been pile-irradiated<sup>7</sup> was dissolved in 25.0 ml. of 8.25 molar hydrochloric acid, oxidized to the ferric state with ceric sulfate, and extracted three times with an equal volume of isopropyl ether. The

iron was won back from the ether by re-extraction with distilled water several times, and finally diluted to 250.0 ml. The efficiency of even a single ether extraction is so high<sup>1</sup> that the tracer solution was assigned a concentration of ferric chloride of 0.02822 molar without further analysis. In view of the 1:1 ratio of hydrochloric acid to ferric chloride in the ether complex, the aqueous hydrochloric acid concentration of the tracer was also considered to be 0.02822 molar. Errors due to slight deviations from these values were negligible, in view of the high hydrochloric acid concentrations in which the tracer was subsequently used. Mixtures of aqueous hydrochloric acid solutions of ferric chloride were then prepared by dispensing standard hydrochloric acid, stock ferric chloride, and tracer ferric chloride into 10.00-ml. glass-stoppered graduated mixing cylinders and diluting accurately to 5.00 ml. with distilled water. 5.00 ml. of permanganate-washed distilled isopropyl ether (b. p. 66.5–67.5° at 746.7 mm.) was then added, and the cylinders transferred to a thermostat controlled to 20.0 ± 0.1°. Mixing of the phases was done by inversion of the cylinders with alternate periods of immersion in the thermostat for an elapsed time of thirty minutes, after which the phases were separated and centrifuged to avoid errors which emulsification would introduce.

Aliquots of from 0.200 to 4.00 ml. of each phase (depending upon the activity of the iron) were evaporated on copper plates having spun-up edges under an infrared lamp. Counting rates of the iron<sup>59</sup> beta activity were determined with a thin wall mica window Geiger-Müller tube and a conventional scaling unit (Instrument Development Laboratories, Model 162 Scaler). Usually a total of 5,000 to 10,000 counts was registered, and the background of the counter was established to be 24.2 c./min. The statistical error in the counting rate did not exceed 2%, and the over-all error (most of which was uncertainty in geometry due to the evaporated residue) was within 5%. No correction was made for self-absorption of the beta particles in the evaporated residue because the energies of the particles are 0.26, 0.46 mev. The material balances obtained were satisfactory, indicating that no serious errors were involved. The equilibrium aqueous and ethereal iron concentrations were calculated by solving sets of simultaneous linear equations of the type:

$$(\text{Fe})_{\text{aq}} + (\text{Fe})_{\text{et}} = (\text{Fe})_{\text{initial}} \quad (3)$$

$$\frac{(\text{Fe})_{\text{et}}}{(\text{Fe})_{\text{aq}}} = \frac{\text{Counting rate ether/ml./min.}}{\text{Counting rate water/ml./min.}} \quad (4)$$

(7) Supplied by Isotopes Branch, United States Atomic Energy Commission, Oak Ridge, Tennessee

Table IV gives the initial ferric chloride and hydrochloric acid concentrations, together with the final iron concentrations and the distribution ratios for iron. Phase volumes were not recorded, since they did not deviate by more than 4% from the initial volumes.

TABLE IV  
DISTRIBUTION OF FERRIC CHLORIDE BETWEEN AQUEOUS  
HYDROCHLORIC ACID AND ISOPROPYL ETHER

(HCl) <sub>i</sub>	(Fe) <sub>i</sub>	(Fe) <sub>aq</sub>	(Fe) <sub>et</sub>	$K = \frac{(Fe)_{et}}{(Fe)_{aq}}$
3.00	0.00339	0.003382	0.00000791	0.00234
3.00	.00865	.0086283	.0000217	.00252
3.00	.02066	.02061	.00004803	.002330
3.00	.02066	.02061	.0000521	.002528
3.00	.06073	.05872	.00201	.03422
3.00	.06073	.06054	.000193	.003193
3.00	.2059	.2039	.00196	.00961
3.00	.2059	.2042	.001715	.0084
3.00	.5064	.4363	.0701	.1606
3.00	.5064	.4310	.07542	.175
4.00	.0002258	.0002157	.0000101	.0468
4.00	.001129	.001073	.0000563	.0525
4.00	.00564	.00545	.000190	.0347
4.00	.02066	.01975	.000914	.0463
4.00	.05171	.04846	.00325	.0670
4.00	.2059	.1402	.0657	.4685
4.00	.4663	.1621	.3042	1.878
5.00	.0002258	.0001626	.0000632	.389
5.00	.001129	.000823	.000306	.370
5.00	.00564	.00434	.00130	.300
5.00	.00564	.003867	.001773	.4585
5.00	.00564	.003824	.001816	.475
5.00	.00865	.00545	.00320	.5875
5.00	.02066	.01660	.00906	.781
5.00	.04370	.01206	.03164	2.621
5.00	.1559	.02184	.1341	6.133
5.00	.3862	.02880	.3574	12.41
6.00	.0002258	.00004207	.0001837	4.367
6.00	.0002258	.00004853	.0001773	3.653
6.00	.001129	.0002532	.000876	3.459
6.00	.00564	.001018	.004622	4.538
6.00	.00564	.001182	.004458	3.771
6.00	.00764	.002121	.00552	2.598
6.00	.00764	.001453	.006187	4.258
6.00	.01566	.002220	.0134	6.050
6.00	.03569	.002205	.03348	15.18
6.00	.1258	.002862	.1229	42.95
6.00	.3061	.00370	.3024	81.69
7.00	.0002258	.000007331	.0002185	29.81
7.00	.0004516	.00001803	.0004336	24.05
7.00	.001129	.00005436	.001075	19.77
7.00	.00564	.0001918	.005448	28.39
7.00	.01072	.0002087	.01051	50.52
7.00	.02567	.0001979	.02547	128.7
7.00	.05572	.0002888	.05543	191.9
7.00	.1058	.0003779	.1054	279.0
7.00	.2059	.000312	.2056	659

There is the possibility that some iron may have been reduced to the ferrous state. Ashley and Murray<sup>8</sup> report

(8) S. E. Q. Ashley and W. M. Murray, *Ind. Eng. Chem., Anal. Ed.*, **10**, 367 (1938).

that iron cannot be completely removed from hydrochloric acid solutions by continuous diisopropyl ether extraction unless performed in the dark, although according to Dodson, Forney and Swift,<sup>2</sup> reduction by alcohol and peroxide impurities in the ether need not be feared.

To eliminate the possibility of photochemical reduction all extractions and separations of phases were performed in subdued artificial light. However, it was deemed desirable to test a number of the aqueous phases for ferrous iron. The Turnbull blue reaction was found to be satisfactory for the purpose. If the acidity of an aqueous phase is neutralized with ammonium hydroxide almost to the point of precipitation of hydrated ferric oxide and a small amount of aqueous potassium ferricyanide added, ferrous iron at concentrations as low as  $10^{-5}$  molar can be detected. At the limit of sensitivity, the color is an olive green rather than blue but can be easily detected, especially if the Turnbull's blue is allowed to flocculate.

A number of analyses of aqueous residues were made. These allow us to place an upper limit of 1% on the fraction of iron which was reduced. The same upper limit obtains on the fraction of iron in the ferrous state in the stock tracer iron solution. This solution had been standing in ordinary laboratory light for fifteen days before the test was made.

By means of this information, we have concluded that error in our equilibrium measurements due to the presence of ferrous iron is less than the other experimental errors involved.

## Discussion B

Figure 4 shows a plot of log ethereal iron concentration against log aqueous iron concentration from the data compiled in Table IV. It is seen that the prediction of constant partition coefficient for a particular hydrochloric acid concentration is fulfilled for sufficiently dilute ferric chloride solutions. Within experimental error, the distribution curves for iron from 3.00, 4.00, 5.00, 6.00 and 7.00 molar hydrochloric acid pass into straight lines of unit slope. Curves of constant total iron concentration appear on the log-log plot for convenience in deducing how a solution having a given total ferric chloride and hydrochloric acid concentration will distribute its iron between the two phases.

Figure 5 is a plot constructed from Fig. 4, showing portions of the bell-shaped distribution curves obtained for varying aqueous hydrochloric acid concentration; the maxima are not shown, since they occur at an acidity (8.5 to 9.0 molar) beyond the range of our experiments. It should be noted that the curves for total iron concentrations up to 0.01 molar coincide rather closely, particularly for lower acidities. The salting-out effect begins to introduce abnormalities for total iron concentrations in the neighborhood of 0.01 molar, and is more pronounced for higher hydrochloric acid concentrations.

Several features of Fig. 4 deserve mention. A decrease in the slope of the log-log curve begins to occur for hydrochloric acid concentrations of 5 molar and above for total iron concentrations above 0.1 molar. It seems likely that all of these curves will show a similar change in slope for sufficiently high iron concentrations, and may even approach the horizontal asymptotically. This would represent a condition of saturation of isopropyl ether by  $HFeCl_4$ , and may explain the ap-

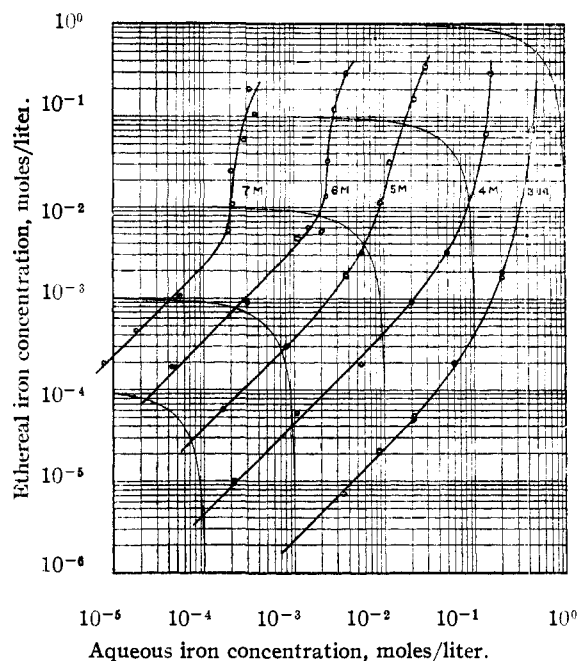


Fig. 4.—Variation of distribution with iron concentration for several hydrochloric acid concentrations.

pearance of a third (ether) iron-rich phase observed by Dodson, Forney and Swift.

It appears to the authors that these data do not preclude the possibility of a polymerized iron complex in solutions of high ferric chloride concentration, but that polymerization is not necessarily the cause of the anomalous distribution. A simple distribution law is followed in systems of low iron concentration, and Beer's law is obeyed for the ether phase over a wide range of iron concentrations<sup>1</sup> which almost overlaps the region of normal behavior. Polymerization therefore appears quite unlikely for ethereal iron concentrations up to 0.4 molar.

### Summary

Data are presented in support of the hypothe-

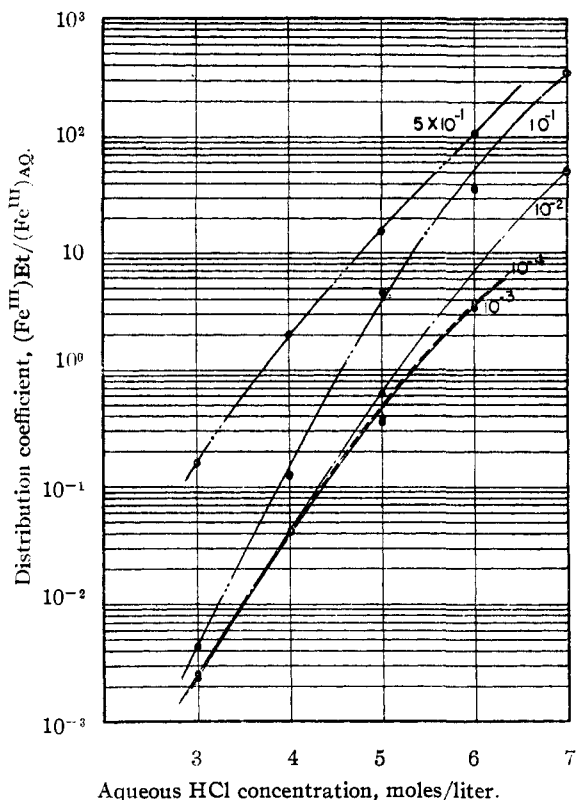


Fig. 5.—Variation of distribution coefficient with hydrochloric acid concentration for several initial ferric chloride concentrations.

sis that a salting-out effect may explain the anomaly in the distribution of ferric chloride between aqueous hydrochloric acid and isopropyl ether. The distribution is found to follow the simple Nernst partition law for systems of low iron concentration. A final decision regarding the status of proposed iron polymers in the ether phase must await activity measurements of the complex in the ether phase and of ferric chloride in hydrochloric acid solutions.

CHICAGO, ILLINOIS

RECEIVED MAY 10, 1948