The action of chlorine gas on neptunium tetrachloride at elevated temperatures failed to yield any higher chlorides of neptunium.

Neptunium tetrabromide was prepared by the action of aluminum bromide on neptunium dioxide, and the tribromide by the same reaction in the presence of excess aluminum.

Neptunium triiodide was prepared by the action of aluminum iodide on neptunium dioxide.

Neptunium metal was prepared by action of barium vapor on neptunium trifluoride at 1200°. The density of the metal was determined.

Neptunium metal was found to react with hydrogen to form a hydride.

The reaction of a hydrogen sulfide–carbon disulfide mixture on neptunium dioxide at 1000° for two hours gave rise to neptunium oxysulfide. Prolonged treatment under the same conditions yielded neptunium sesquisulfide.

Ignition of Np(IV) nitrate in 28 atmospheres of oxygen at 400° did not produce a higher oxide of neptunium. Under the same conditions U_3O_8 is converted to UO_3.

Some regularities in the stabilities of compounds of uranium, neptunium and plutonium in their different oxidation states are pointed out.

CHICAGO, ILL. RECEIVED APRIL 12, 1948

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

The Extraction of Ferric Chloride by Isopropyl Ether. I

BY NORMAN H. NACHTRIEB[1] AND JOHN G. CONWAY[2]

This is the first of several papers in which an account is given of experiments on the extraction of ferric chloride from aqueous hydrochloric acid solutions by diisopropyl ether. Although the extraction has received considerable attention since its discovery by Rothe over fifty years ago[3] a complete explanation of the phenomenon has not yet been given. A considerable number of papers have described applications of the extraction to the separation of iron from other elements in chemical analysis.[4,5,6,7] The extraction is of interest for its own sake, however, for as pointed out by Dodson, Forney and Swift[8] the partition coefficient is a function of the total iron concentration. Sandell[9] also calls attention to this anomaly, in which the efficiency of extraction of ferric chloride by diethyl ether increases with increasing total iron concentration. Kato and Ishii[10] reported the empirical formula of the ether-extracted compound to be $2[FeCl_3 \cdot HCl] \cdot 9H_2O \cdot 15(C_2H_5)_2O$ and proposed a structure for a dimeric molecule in which chlorine was considered to occupy positions corresponding to the apices of tetrahedra around central iron atoms; water molecules were considered to lie along the edges of the tetrahedra with such an orientation as to minimize the dipole moment of the molecule. Axelrod and Swift[11] reported the empirical formula of the iron salt extracted by β,β'-dichlorodiethyl ether as $HFeCl_4 \cdot 4.5H_2O$ and also suggested that the ethereal iron complex was a dimer.

In this first paper general observations are reported on the rate of attainment of equilibrium, the analysis of the ether phase for iron, chloride, ionizable hydrogen and water, the variation of the distribution coefficient with aqueous hydrochloric acid concentration, the temperature dependence of the distribution coefficient, and the absorption spectrum of the ether phase in the visual region.

Experimental

By and large, the analytical procedures of Dodson, Forney and Swift[8] were used. Technical grade isopropyl ether was shaken with alkaline potassium permanganate to destroy peroxides, dried over calcium chloride, and distilled. The fraction boiling between 60.0 and 60.1° at 587.9 mm. was reserved for use. Stock solutions of ferric chloride were prepared from reagent grade $FeCl_3 \cdot 6H_2O$ and standardized by the Zimmerman–Reinhardt and Volhard procedures.[12]

Free acid was calculated from titrations with standard sodium hydroxide by allowing for the quantity of base consumed in the precipitation of iron as hydrated ferric oxide. All extractions were carried out in 100-ml. glass-stoppered cylinders with 50.0 ml. of isopropyl ether and 50.0 ml. of aqueous solution of known ferric chloride and hydrochloric acid concentrations, except as noted. Unless otherwise indicated the extractions were carried out at 25.0 ± 0.1°.

Ether phase aliquots were shaken with distilled water and the determinations of iron and acidity performed on the solutions so derived; this obviated the necessity of removing the ether by distillation and simplified analysis. Macro concentrations of iron were determined by the Zimmerman–Reinhardt procedure, as stated; trace concentrations of iron were determined spectrophotometrically with ortho-phenanthroline.[13] Hydrogen chloride concentrations were calculated by subtracting three times

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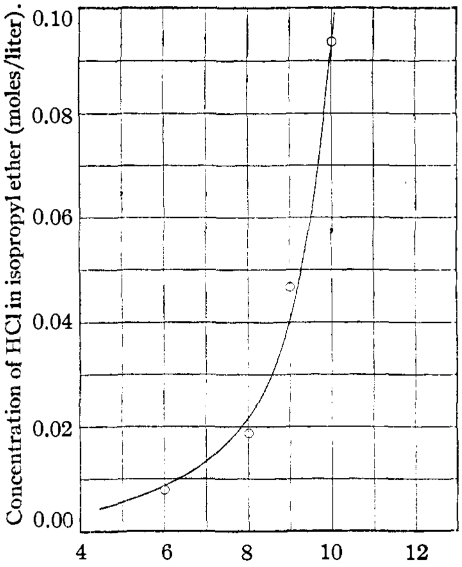

Fig. 1.—Solubility of hydrochloric acid in isopropyl ether.

the ferric iron concentration (moles per liter) previously determined, from the total number of milliequivalents of standard sodium hydroxide required per milliliter of the aliquot; phenolphthalein was the indicator used. Hydrogen chloride concentrations in the ether phase were corrected for the solubility of aqueous hydrochloric acid in isopropyl ether (Fig. 1).

Determination of the quantity of water extracted by the ether along with the iron was accomplished by a modified Zerewitinoff method,[14] using methylmagnesium iodide. The volume of methane liberated by an aliquot of an ether phase when added to an excess of the Grignard reagent was corrected for the volume produced by the water and hydrogen chloride in hydrochloric acid-saturated isopropyl ether and for the quantity produced by the hydrogen chloride associated with the extracted iron compound. Bureau of Standards benzoic acid, dried at 95°, was used to check the accuracy of the method for available hydrogen. Found: 0.841, 0.814, 0.839% acid hydrogen. Theoretical: 0.825%.

Absorption spectrum measurements were made with 1.00-cm. cells in a Beckman quartz spectrophotometer.

Discussion of Results

Rate of Attainment of Equilibrium.—The rate with which equilibrium is approached in the extraction of ferric chloride depends to a very great extent upon the degree of emulsification of ether in hydrochloric acid which results from mixing. Control over the degree of emulsification is difficult to obtain when mixing is carried out by manual inversion of the cylinders, and the results obtained have significance only for extractions performed in this manner. Four solutions were thermostatted to 25.0 ± 0.1° and alternately mixed by inversion and thermostatted for one minute intervals for elapsed times of five, ten, twenty and forty minutes, respectively. Inversion was at such a rate as just to permit the air bubble in the cylinders to traverse the length of the chamber. Figure 2 shows the change in the distribution ratio with time for a solution which was initially 1.323 *M* ferric chloride and 10.66 *M* hydrochloric acid. On the basis of several experiments of this type a mixing time of thirty minutes was adopted for succeeding experiments.

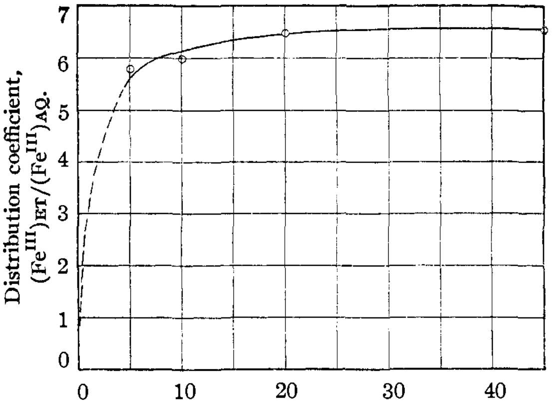

Fig. 2.—Rate of approach to extraction equilibrium.

Analysis of the Ether Phase.—A series of extractions was made for an initial ferric chloride concentration of 0.853 *M* in hydrochloric acid of concentration ranging from 2 to 10 *M*. Analysis of aliquots of the ether phases for iron, chloride, and ionizable hydrogen gave the results shown in Table I. The values given for ethereal hydrogen and chloride have been corrected for the solubility of hydrochloric acid in isopropyl ether by means of Fig. 1. Examination of the empirical formulas tabulated in the last column shows that essentially equimolecular quantities of ferric chloride and hydrogen chloride are co-extracted out of aqueous solutions initially less than 8 *M* hydrochloric acid. These formulas were calculated from the iron and acidity determinations. For higher initial hydrochloric acid concentrations an increasingly greater quantity of hydrogen chloride is co-extracted. It is not clear whether this should be interpreted as a "salting in" effect caused by ferric chloride or to indicate the formation of mixtures of higher complexes of the type: H_2FeCl_5, H_3FeCl_6, etc. Since the absorption spectrum of the ether phase does not alter noticeably when more than the stoichiometric ratio of hydrogen chloride is present, it seems likely that the effect is merely one of anomalous solubility. The accuracy of the ethereal chloride determination leaves something to be desired, but confirms the one to four mole ratio of iron or hydrogen to chloride and indicates that the complex contains no other negative constituents. An average of twenty-eight analyses of ether phases of extractions from hydrochloric acid of less than eight molar gives as the empirical formula: $H_{0.98 \pm 0.054}FeCl_{3.98 \pm 0.054}$. This formula is based upon Zimmermann-Reinhardt determinations for iron and total neutralization equivalent. Table II shows the results of the determinations of the quantity of

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TABLE I

ANALYSES OF AQUEOUS AND ETHEREAL PHASES

$[HCl]_i$	$[FeCl_3]_i$	$[Fe]_{aq}$	$[Fe]_{et}$	$[Cl]_{aq}$	$[Cl]_{et}$	$[H]_{aq}$	$[H]_{et}$	V_{aq}, cc.	V_{et}, cc.	$[Fe]_{et}/[Fe]_{aq}$	Empirical formula (ether)[c]
2.00	0.853	0.831	0.0069	4.351	0.0218	1.720	0.00664	51.0	49.0	0.0083	$FeCl_3 \cdot 0.96HCl$
3.00	.853	.620	.2506	4.592	.899	2.783	.2420	49.0	50.3	.405	$FeCl_3 \cdot 0.97HCl$
4.00	.853	.3465	.507	4.215	1.890	3.670	.529	46.3	52.7	1.46	$FeCl_3 \cdot 1.04HCl$
5.00	.853	.1178	.709	4.921	2.598	4.640	.664	45.0	54.0	6.01	$FeCl_3 \cdot 1.00HCl$
6.00	.853	.02255	.780	5.464	2.830	5.830	.840	44.5	53.6	34.6	$FeCl_3 \cdot 1.08HCl$
7.00	.853	.003265	.805	6.377	3.180	6.520	.905	45.0	53.3	246	$FeCl_3 \cdot 1.12HCl$
8.00	.853	.001062	.815	...	3.53	7.89	1.58	..	..	767	$FeCl_3 \cdot 1.94HCl$
9.00	.853	.0006343	.837	...	3.87	7.90	1.64	..	..	1320	$FeCl_3 \cdot 1.96HCl$
10.00	.853	.001480	.830	...	5.03	8.01	2.81	46.6	50.9	560	$FeCl_3 \cdot 3.40HCl$
5.75	.334	.0167	.326	5.017	1.250	5.530	0.350	48.7	50.0	19.5	$FeCl_3 \cdot 1.07HCl$
5.91	.663	.0135	.627	5.577	2.510	5.590	.540	46.0	52.8	46.5	$FeCl_3 \cdot 0.86HCl$
5.47	.1804	.0186	.166	5.201	0.615	5.210	.171	49.8	49.1	8.93	$FeCl_3 \cdot 1.03HCl$
6.025	1.322	.1662	1.074[b]	5.251	4.170	5.620	1.074	20.0[a]	28.4	6.46	$FeCl_3 \cdot 1.00HCl$
6.025	1.324	.1638	1.071	5.247	4.260	5.600	1.014	21.0[a]	28.0	6.55	$FeCl_3 \cdot 0.95HCl$
11.00	0.853	.00456	0.815	...	5.450	10.01	3.293	..	..	179	$FeCl_3 \cdot 4.04HCl$

[a] Initial volumes: 25.0 ml. aqueous; 25.0 ml. isopropyl ether. [b] Optical density = 0.741 for 1 cm. path, λ = 530 millimicrons. [c] Empirical formulas calculated from iron and hydrogen ion determinations. Subscripts: i = initial (moles/liter): aq = final aqueous (moles/liter); et = final ether (moles/liter).

TABLE II

WATER ASSOCIATED WITH ETHER-EXTRACTED IRON COMPLEX

Initial HCl molarity	$[H]_{et}$	$[Fe]_{et}$	$[Cl]_{et}$	Cc. CH_4 per ml. ether, N. T. P.[a]	Empirical formula
6.00	0.9069	0.7995	3.160	208.8	$FeCl_3 \cdot 1.13HCl \cdot 10.52H_2O$
6.00	.0337	.0427	0.1443	9.9	$FeCl_3 \cdot 0.79HCl \cdot 9.6H_2O$
7.50	.966	.834	3.416	223	$FeCl_3 \cdot 1.16HCl \cdot 10.78H_2O$
8.25	.0723	.0553	0.240	14.4	$FeCl_3 \cdot 1.31HCl \cdot 10.30H_2O$
9.00	1.675	.8316	3.936	261	$FeCl_3 \cdot 2.01HCl \cdot 12.00H_2O$
10.00	1.922	.879	4.440	303	$FeCl_3 \cdot 2.19HCl \cdot 13.20H_2O$
10.00	0.0837	.0277	0.1753	8.5	$FeCl_3 \cdot 3.02HCl \cdot 10.70H_2O$

[a] Methane produced by aliquot of ether saturated with hydrochloric acid of same concentration subtracted as blank.

water associated with the iron complex extracted by ether. The volumes of methane tabulated have been corrected for solubility of water and hydrochloric acid dissolved in isopropyl ether by means of blank runs, and have been reduced to standard conditions. Again, it is not clear whether the water found should be interpreted as constitutional, or whether it is due to enhanced solubility caused by the ferric chloride.

Variation of Distribution Coefficient with Aqueous Hydrochloric Acid Concentration.—Figure 3 is a plot of the distribution coefficients of Table I for 0.853 *M* ferric chloride for various initial hydrochloric acid concentrations; the square points on the same figure pertain to the equilibrium hydrogen ion concentration. It is a consequence of the dependence of the partition coefficient upon the total iron concentration (noted earlier by Dodson, Forney and Swift) that this is but one of a family of similar bell-shaped curves, each for a given initial iron concentration. It should be noted that the curve for the equilibrium hydrogen ion concentration does not extend beyond eight molar. For hydrochloric acid concentrations initially above eight molar the equilibrium aqueous acid concentration does not increase materially.

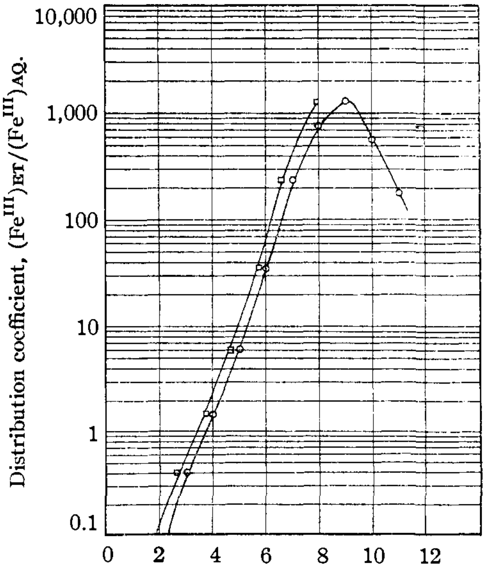

Fig. 3.—Variation of distribution coefficient with hydrochloric acid concentration.

Temperature Dependence of the Partition Coefficient.—A series of extractions of 0.9595

TABLE III

TEMPERATURE DEPENDENCE OF DISTRIBUTION COEFFICIENT

t, °C.	$[HCl]_i$	$[FeCl_3]_i$	$[Cl]_{aq}$	$[Cl]_{et}$	$[Fe]_{aq}$	$[Fe]_{et}$	$[H]_{aq}$	$[H]_{et}$	$[Fe]_{et}/[Fe]_{aq}$	V_{aq}, cc.	V_{et}, cc.
0.00	3.50	0.9595	4.387	2.233	0.416	0.570	3.165	0.538	1.370	46.0	49.5
10.50	3.50	.9595	4.426	2.091	.439	.541	3.109	.487	1.233	46.5	50.8
20.80	3.50	.9595	4.583	2.002	.467	.504	3.150	.494	1.079	47.0	51.0
29.95	3.50	.9595	4.659	1.801	.505	.467	3.131	.440	0.925	46.5	52.2
38.30	3.50	.9595	...	1.686	.514	.462	3.145	.450	.899	46.7	52.3

M ferric chloride in 3.500 *M* hydrochloric acid was carried out at five different temperatures. Table III shows the equilibrium concentrations found, together with the phase volumes and distribution ratios. Figure 4 is a plot of $R \log_e (\text{Fe})_{et}/(\text{Fe})_{aq}$ against $1/T$. To the extent that the distribution ratio is proportional to the over-all thermodynamic equilibrium constant for the extraction, this application of the van't Hoff equation is valid and the slope of the curve is the negative of the partial molar heat of extraction

$$\Delta H = -1970 \text{ cal. mole}^{-1}$$

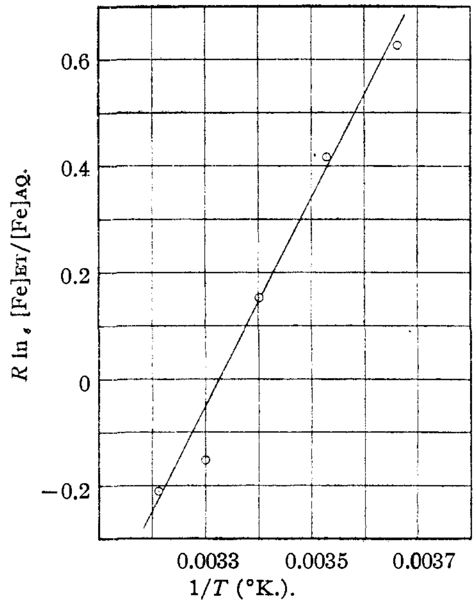

Fig. 4.—Heat of extraction of ferric chloride by isopropyl ether.

More exactly, the van't Hoff equation is written

$$\frac{d \ln K}{dT} + \sum \frac{d \ln \gamma_E/\gamma_A}{dT} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant measured in terms of concentration and γ_i are the activity coefficients for the various components in the two phases. Each activity coefficient varies with temperature as

$$\frac{d \ln \gamma_i}{dT} = \frac{-\bar{L}}{RT^2}$$

where $\bar{L}$ is the heat of dilution from any given concentration to infinite dilution.

These $\bar{L}$'s are included in the ΔH determined from Fig. 4, and hence the temperature dependence of the concentration equilibrium constant does not determine the heat of extraction unless the various $\bar{L}$ terms cancel.

Absorption Spectrum of the Ether Phase.—Figure 5 shows the absorption spectra of (1) aqueous ferric chloride, (2) aqueous ferric chloride in 7.5 molar hydrochloric acid, (3) the ether-extracted iron complex and (4) anhydrous ferric chloride in isopropyl ether. The strong absorption at 410 millimicrons is a feature common to all four spectra, having therefore, no significance for the ethereal iron complex, itself. The absorption maxima at 532, 618 and 685 millimicrons are characteristic of the ether-extracted complex, however. All of these (including the arbitrarily selected wave length, 725 millimicrons) appear to follow Beer's law, as shown by Fig. 6. The extinction–concentration relationships are linear, and the curves pass through the origin within experimental error. The fact that Beer's law is followed for four different wave lengths over such a wide range of iron concentrations (0.01 to 0.4 *M*) makes it extremely unlikely that several species of iron complex coexist in the ether phase. The very weak maximum at 512 millimicrons and the

TABLE IV

ABSORPTION SPECTRUM EXTINCTION COEFFICIENTS OF ETHER PHASE

$(Fe)_{et}$(m./l.)	Optical density[a] 532 mμ	618 mμ	685 mμ	725 mμ
0.00902	0.012	0.004	0.007	0.0095
.0182	.0255	.008	.012	.014
.0278	.0375	.012	.018	.0185
.0485	.063	.019	.030	.0275
.0971	.1265	.043	.062	.050
.1932	.251	.078	.116	.088
.2740	.3665	.1145	.168	.124
.3991	.531	.164	.240	.176
.00396[b]	.009	.006	.006	.005
.00730[b]	.014	.007	.008	.007
.02146[b]	.030	.012	.016	.012
.1123[b]	.145	.050	.074	.052
.1984[b]	.252	.084	.126	.089
.3840[b]	.484	.160	.242	.170
Average molar extinction coefficient (moles^{-1} cm^{-1} liters)	1.44 ± .20	0.55 ± .20	0.75 ± .17	0.65 ± .21

[a] Quartz cells, 1.000 cm. in length. Pure isopropyl ether as reference. [b] Values obtained five months later with different ether solutions.

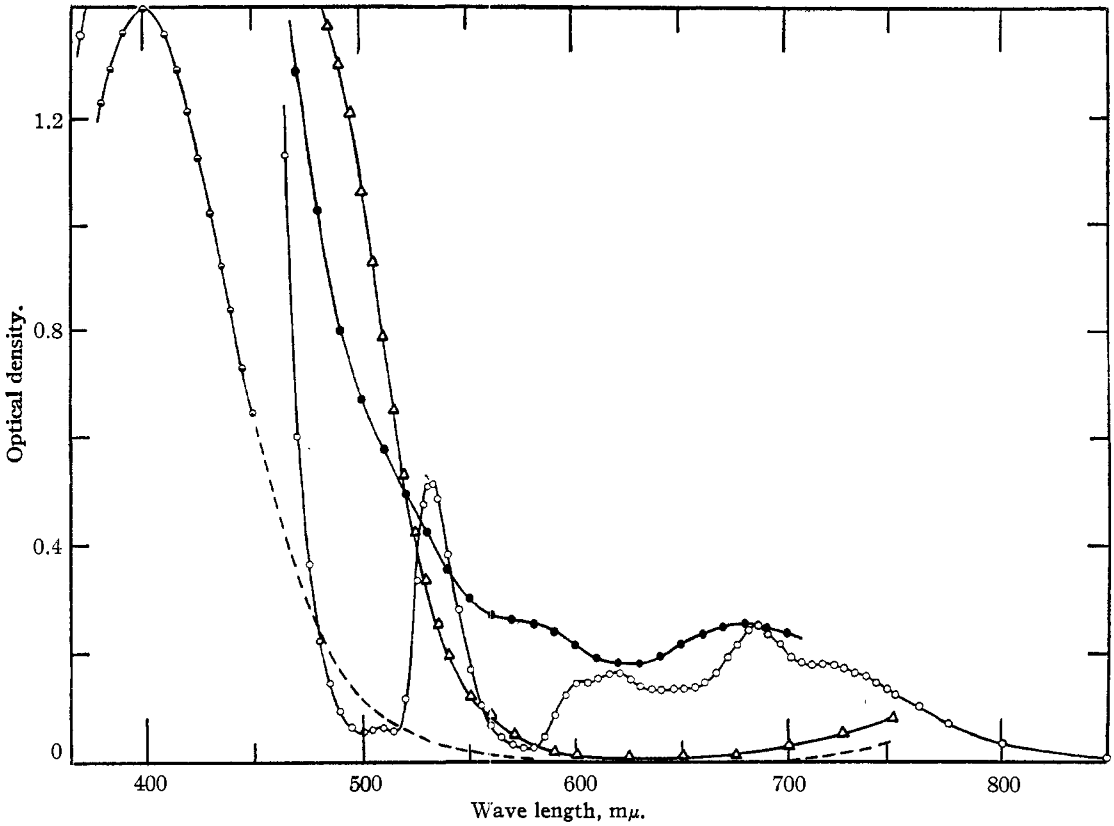

Fig. 5.—Absorption spectra of iron chlorides: ●, 0.32 *m* $FeCl_3$ in isopropyl ether; ⊖, 0.05 *m* aqueous $FeCl_3$; ○, 0.40 *m* $HFeCl_4$ in isopropyl ether; △, 0.05 *m* $FeCl_3$ in 7.5 *m* hydrochloric acid.

unresolved bands at 716 and 608 millimicrons (Fig. 5) are features of the ethereal iron complex spectrum which have not been investigated. Anhydrous ferric chloride in isopropyl ether has an

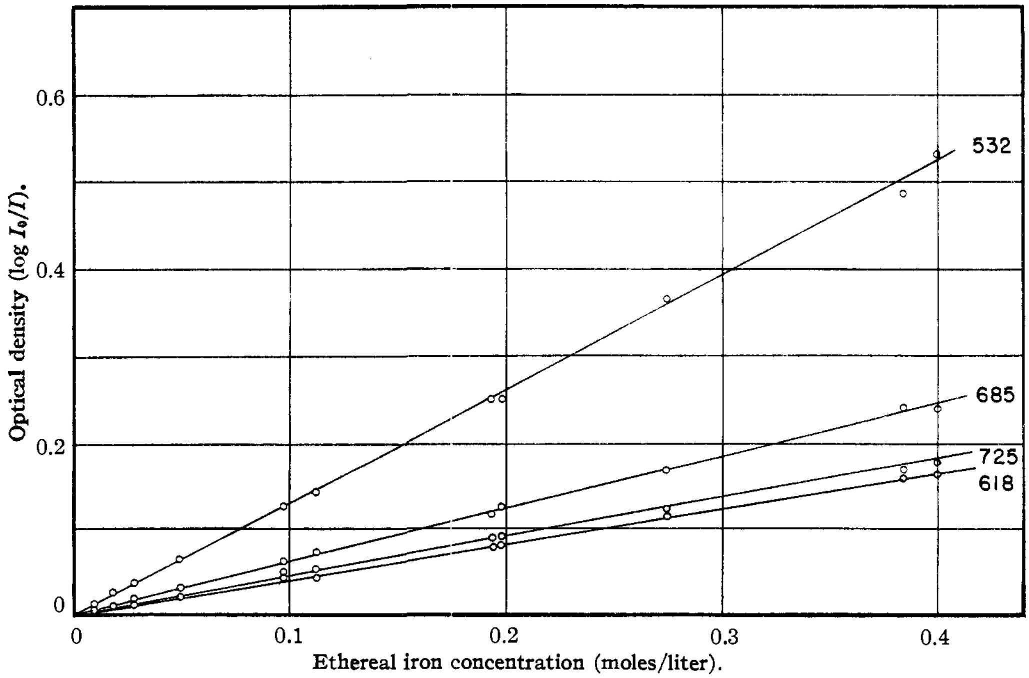

Fig. 6.—Beer's law conformity of ethereal $HFeCl_4$ solutions.

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 $HFeCl_4$. For aqueous hydrochloric acid concentrations exceeding 8 molar the mole ratio of hydrogen chloride to ferric chloride exceeds 1:1. Determinations of water co-extracted with $HFeCl_4$ 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,[1] adds experimental evidence to the observation of Dodson, Forney and Swift[2] 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 $HFeCl_4$ in isopropyl ether must be obtained before equilibrium calculations which have any meaning may be made. Axelrod and Swift,[3] 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[4] and by Axelrod and Swift[3] (of β,β'-dichlorodiethyl ether) indicated a mole ratio $(H_2O)/(Fe)$ 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 $HFeCl_4$ 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 $HFeCl_4$ 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

$$n\mathrm{Fe}^{+3}_{\mathrm{aq}} + n\mathrm{H}^{+}_{\mathrm{aq}} + 4n\mathrm{Cl}^{-}_{\mathrm{aq}} \rightleftarrows (\mathrm{HFeCl_4})_{n\ \mathrm{et}}$$

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

$$\begin{gathered}
\mathrm{Fe}^{+3}_{\mathrm{aq}} + \mathrm{Cl}^{-}_{\mathrm{aq}} \rightleftarrows \mathrm{FeCl}^{+2}_{\mathrm{aq}} \\
\mathrm{FeCl}^{+2}_{\mathrm{aq}} + \mathrm{Cl}^{-}_{\mathrm{aq}} \rightleftarrows \mathrm{FeCl_2}^{+1}_{\mathrm{aq}} \\
\vdots \qquad \vdots \qquad \vdots \\
\mathrm{FeCl_4}^{-}_{\mathrm{aq}} + \mathrm{H}^{+}_{\mathrm{aq}} \rightleftarrows \mathrm{HFeCl}_{4\,\mathrm{aq}} \\
n\mathrm{HFeCl}_{4\mathrm{aq}} \rightleftarrows (\mathrm{HFeCl_4})_{n\ \mathrm{et}}
\end{gathered}$$

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

$$(\mathrm{Fe})_{n\ \mathrm{et}}/(\mathrm{Fe})^{n}_{\mathrm{aq}} = K_{(\mathrm{H}^+).(\mathrm{Cl}^-)\ \mathrm{const.}} \qquad (1)$$

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

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

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