tion of the theory of polarographic currents controlled by rate of reaction and by diffusion.

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The Extraction of Ferric Chloride by Isopropyl Ether. III[1]

BY NORMAN H. NACHTRIEB AND ROBERT E. FRYXELL[2]

Stoichiometric activity coefficients have been determined by an e.m.f. cell method for ferric chloride in 5 F HCl saturated with $FeCl_2 \cdot 4H_2O$. On the basis of these measurements it is concluded that the abnormal extraction of ferric chloride by isopropyl ether is the result of low activity coefficients for the salt in the ether phase. The appearance of a third liquid phase is shown to arise from the same cause.

Two interpretations have been offered to account for deviations from the Nernst distribution law shown by the ferric chloride:isopropyl ether extraction system. Kato and Ishii[3] and Swift and co-workers,[4,5] on the one hand, have maintained that the iron-bearing compound extracted by ethers undergoes polymerization as the aqueous ferric concentration is increased. The latter investigators assumed essentially ideal behavior of ferric chloride in the aqueous phase and calculated effective polymerization numbers for the ethereal iron complex. Their isopiestic measurements, made on ethereal iron solutions, supported this view although the experiments were only semi-quantitative. Nachtrieb, Fryxell and Conway,[6,7] on the other hand, have proposed that deviations of the aqueous ferric chloride phase from dilute solution laws may be responsible for the apparent failure of the distribution law. This proposal was based primarily upon the adherence of absorption bands of the ethereal solutions to Beer's law over a range of iron concentration which extended well into the region of anomalous extraction.

A choice between these opposing interpretations can be made by measurement of some thermodynamic property of ferric chloride in either phase as a function of the concentration of trivalent iron in that phase. Isopiestic experiments reach equilibrium only slowly and are difficult to interpret in a 4-component system (ferric chloride, hydrogen chloride, water and isopropyl ether) when three of the components are volatile. The authors have therefore attempted to determine the variation in the activity coefficient of ferric chloride in the aqueous phase by an e.m.f. method. In order to do this it has been necessary to introduce a fifth component (ferrous chloride) into the system to permit the use of a cell with a ferrous ferric
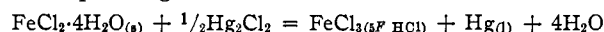
electrode. Although the system has been made more complex thereby the conclusions drawn are believed to apply to the simpler extraction system. As will be seen, the stoichiometric activity coefficient of aqueous ferric chloride does not deviate significantly from unity over the concentration range concerned. By implication, then, the cause of the abnormal distribution is a remarkable decrease in the activity coefficient of ferric chloride in the ether phase, in agreement with the interpretation of Swift and his co-workers.

E.m.f. Measurements

The cell studied was

$$Pt/FeCl_2 \cdot 4H_2O/FeCl_{3(xF)} + HCl_{(5F)}/HCl_{(5F)}/Hg_2Cl_2/Hg \tag{1}$$
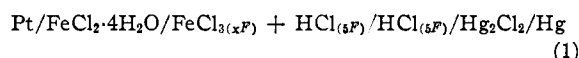
corresponding to the cell reaction

$$FeCl_2 \cdot 4H_2O_{(s)} + {}^1\!/_2 Hg_2Cl_2 = FeCl_{3(5F\ HCl)} + Hg_{(l)} + 4H_2O$$

Three of the cell components are pure substances ($FeCl_2 \cdot 4H_2O$, Hg_2Cl_2 and Hg) and are therefore at constant activity. The activities of water and of ferrous chloride are not separately fixed, but for the purposes of this experiment probably do not vary appreciably. The activity of $FeCl_2 \cdot 4H_2O$ is constant, but the formal solubility in 5 F HCl at 25° varies with ferric chloride concentration according to the equation: Solubility $= 1.75 - 0.85 [Fe^{III}]$. This equation gives the ferrous chloride solubility to ± 0.01 F for ferric chloride concentrations up to 0.5 F. Thus, at constant hydrochloric acid activity the e.m.f. of the cell varies with the concentration of ferric chloride according to the equation

$$E = E^0 - \frac{RT}{F} \ln [FeCl_3] - \frac{RT}{F} \ln \gamma_{FeCl_3}$$

where $[FeCl_3]$ is the stoichiometric ferric iron concentration expressed in formula weights per liter and γ_{FeCl_3} is the stoichiometric activity coefficient for ferric chloride.

Figure 1 shows the cell. The calomel reference electrode (A) made contact with the cell solution through a capillary (B) which was flushed before each experiment with 5.00 F HCl from the reservoir (C). Nitrogen, purified by passage over finely divided copper at 245° was admitted through (G) and removed through (H) to prevent oxidation of ferrous chloride. The temperature was maintained at 25.0 $\pm$ 0.1° by circulating thermostated water through the cell jacket. Magnetic stirring ensured thorough mixing of the

(1) Abstracted from a dissertation submitted by Robert E. Fryxell to the Department of Chemistry of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) General Electric Company, Pittsfield, Massachusetts.

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

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

(5) R. J. Meyers, D. E. Metzler and E. H. Swift, *ibid.,* **72**, 3767 (1950); R. J. Meyers and D. E. Metzler, *ibid.,* **72**, 3772 (1950); D. E. Metzler and R. J. Meyers, *ibid.,* **72**, 3776 (1950).

(6) N. H. Nachtrieb and J. G. Conway, *ibid.,* **70**, 3547 (1948).

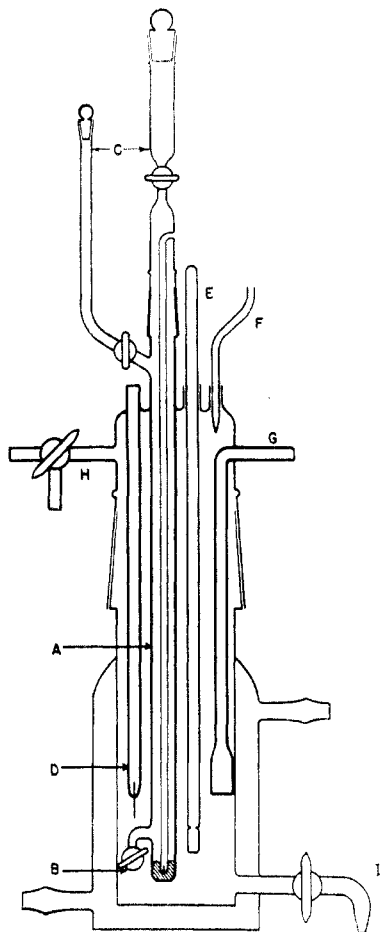(7) N. H. Nachtrieb and R. E. Fryxell, *ibid.,* **70**, 3552 (1948).

Fig. 1.—E.m.f. cell.

solutions and saturation with ferrous chloride. Measured volumes of saturated ferrous chloride in 5 F HCl could be introduced at (F) through a Walden reductor, and known volumes of the electrolyte could be withdrawn at (I).

A saturated ferrous chloride solution in 5.00 F HCl containing a high concentration of ferric chloride was placed in the cell. A quantity of freshly washed $FeCl_2 \cdot 4H_2O$ crystals was then introduced and the cell was purged with nitrogen. After the e.m.f. attained a stable value[8] an accurately measured volume of the electrolyte was withdrawn and aliquots were reserved for analysis. An equal volume of saturated ferrous chloride in 5.00 F HCl was then added through the silver reductor and the stable e.m.f. again recorded. This process was continued until the ferric chloride concentration was reduced to $< 10^{-5}$ F.

Ferrous iron concentration was determined immediately after withdrawal of the solution by permanganate titration in the presence of Zimmerman–Reinhardt preventive solution at 0°. Total iron concentration was determined in the same way after passage of another aliquot through a Jones reductor. The higher ferric iron concentrations were calculated by difference; the dilution ratio was used to calculate concentrations of ferric iron too low to determine accurately by difference. Chloride concentration was determined gravimetrically as silver chloride. Hydrochloric acid concentration was calculated as the difference between chloride and the chloride associated with ferrous and ferric iron.

For the purpose of referring all measurements to the hydrogen scale the e.m.f. of the cell

$$Hg_{(l)}/Hg_2Cl_{2(s)}/HCl_{(5F)}/H_{2(1\ atm.)}/Pt \qquad (2)$$
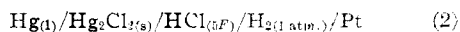
was determined in the same apparatus by inserting a platinum black electrode in tube (G) and re-

(8) Measurements were made for periods of 40 to 50 minutes, although a steady value was reached almost immediately.

placing the electrolyte with 5.00 F HCl. The e.m.f. of the cell

$$Pt/H_{2(1\ atm.)}/HCl_{(5F)}/HCl_{(a-1)}/H_{2(1\ atm.)}/Pt \qquad (3)$$
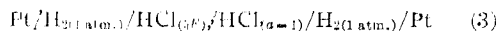
was calculated from the data of Åkerlöf and Teare.[9] The sum of the e.m.f.'s for cells (2) and (3) is -0.1959_1 volt. This value, added to the measured e.m.f. values for cell (1) gives the magnitude of the ferrous–ferric potential in 5 F HCl referred to the hydrogen scale.[10] The e.m.f.'s of the cell

$$Pt/FeCl_2 \cdot 4H_2O_{(s)}/FeCl_{3(x\ F)} + HCl_{(5F)}/HCl_{(a-1)}/H_{2(1\ atm.)}/Pt \qquad (4)$$
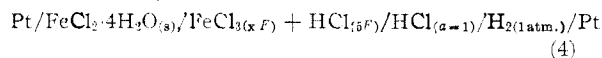
so computed are plotted in Fig. 2, together with the theoretical curve (calculated for $\gamma_{FeCl_3} = 1$ over the entire concentration range). The theoretical Nernst slope is very closely followed from about 5×10^{-3} to 0.2 F ferric chloride. For concentrations lower than 5×10^{-3} F some oxidation of ferrous iron occurs, increasing the actual concentration of ferric iron above its nominal value, and the experimental curve begins to approach a horizontal asymptote.[11]
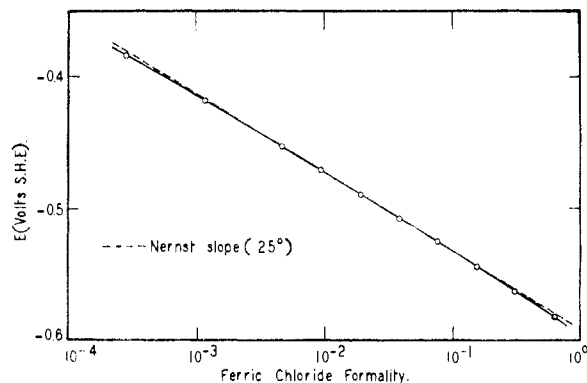

Fig. 2.

## Aqueous Ferric Chloride Activity Coefficients

The e.m.f. of cell (4) at 25.0° may be expressed by the equation $E = E^0 - 0.05916 \log [FeCl_3] - 0.05916 \log \gamma_{FeCl_3}$. This may be rewritten as $0.05916 \log \gamma_{FeCl_3} = E^0 - (E + 0.05916 \log [FeCl_3])$, and the quantity enclosed by parentheses defined as $E^{0\prime}$. A plot of $E^{0\prime}$ versus some function of the ferric chloride concentration gives E^0 in the limit of zero ferric chloride concentration. The extrapolation of $E^{0\prime}$ to its limiting value at zero ferric chloride concentration has been made with zero slope, rather than according to the Debye–Hückel limiting law, because the ionic strength approaches the high value of the mixed solvent instead of zero. The value of E^0 obtained from Fig. 3 (-0.5906) is the standard potential of the saturated ferrous chloride:ferric chloride electrode in 5.00 F HCl referred to the hydrogen scale.

Substitution of the value for E^0 into the equation gives values for the stoichiometric activity coefficient of ferric chloride (in 5.00 F HCl saturated with $FeCl_2 \cdot 4H_2O$) which are plotted in Fig. 4.

(9) G. Åkerlöf and J. W. Teare, THIS JOURNAL, **59**, 1855 (1937).

(10) The Lewis and Randall sign convention has been used throughout.

(11) The equilibrium concentration of ferric iron after passage through the silver reductor has been calculated as approximately 10^{-8} F.
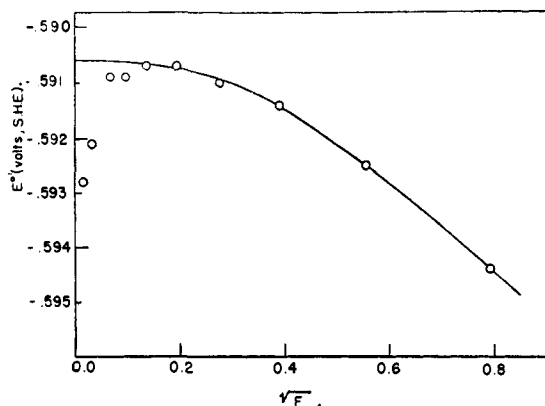
Fig. 3.—$E^{o'}$ function for the aqueous phase.

No claim is made for high accuracy in these values, in view of the uncertainty with which the activity of water is known at high concentrations of ferric chloride. Clearly, however, the deviations of these activity coefficients from unity are far too small to account for the anomalous extraction, even if the water activity does vary within reasonable limits.
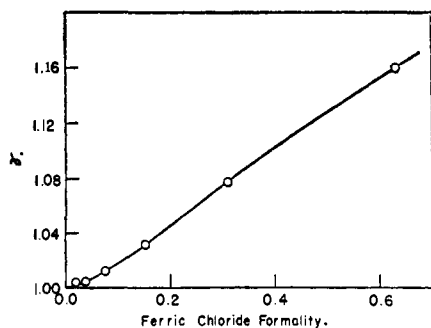
Fig. 4.—Activity coefficient for ferric chloride in 5.00 formal HCl saturated with $FeCl_2 \cdot 4H_2O$.

Ethereal Ferric Chloride Activity Coefficients

Since the activity coefficients for aqueous ferric chloride are now known the activity coefficients for ethereal ferric chloride are readily calculated from distribution coefficients for the 5 component system. Distribution coefficients for ferric chloride between isopropyl ether and 5.00 F HCl saturated with ferrous chloride were determined in the manner previously described. These data, together with the corresponding data for the system without ferrous chloride are plotted on logarithmic coördinates in Fig. 5. Figure 6 shows a plot of the stoichiometric activity coefficient for ethereal ferric chloride obtained from Fig. 2 and 5 by use of the equation $\gamma_{FeCl_3(et)} = 22.0 \; \gamma_{FeCl_3(aq)}/K$, where K is the distribution coefficient, $[FeCl_3]_{et}/[FeCl_3]_{aq}$ and 22.0 is the limiting value of K at 25.0° at infinite dilution in 5 F HCl saturated with $FeCl_2 \cdot 4H_2O$. Since the solubility of ferrous chloride in isopropyl ether is very low it is clear that the ethereal ferric chloride activity coefficients apply equally to the 4- and 5-component systems.

Ether Phase E.m.f. Measurements

A test of the self-consistency of ethereal ferric chloride activity coefficients calculated from e.m.f. data for the aqueous phase and distribution coefficients is the direct measurement of the e.m.f. of cells with ether phase electrolytes.
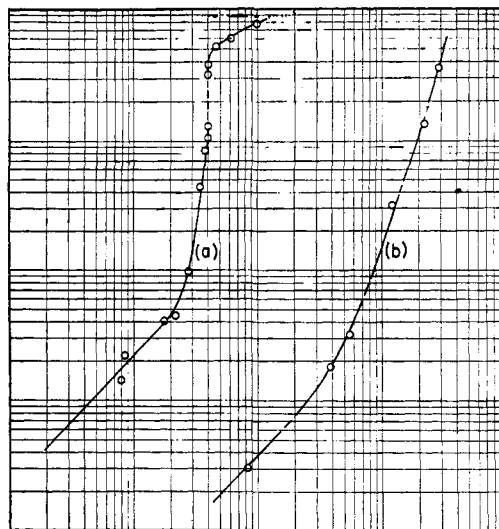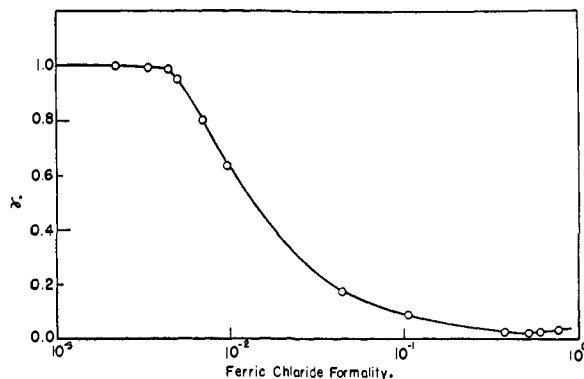

Fig. 5.—Variation of distribution with ferric chloride concentration for 5.00 F hydrochloric acid: (a) in presence of saturated $FeCl_2 \cdot 4H_2O$; (b) in absence of $FeCl_2 \cdot 4H_2O$.

Fig. 6.—Activity coefficient for ferric chloride in the ether phase.

The cell studied was the same as cell (1), except that the hydrochloric acid concentration was in equilibrium with aqueous 5 F HCl saturated with ferrous chloride and containing ferric chloride. The same experimental arrangement was used. Fifty ml. of isopropyl ether was added to 50 ml. of aqueous hydrochloric acid saturated with ferrous chloride and containing varying concentrations of ferric chloride. The initial aqueous hydrochloric acid concentrations were selected so as to furnish an equilibrium acid concentration of 5 F after extraction of the ferric chloride. Only those experiments were accepted for which analysis later showed the equilibrium aqueous acid concentration to lie between 4.90 and 5.10 F. E.m.f. measurements were made first with the electrodes immersed in the aqueous phase. Solution was then drained from the cell until the electrodes were immersed in the ether layer, and the e.m.f. of the cell was redetermined. Aliquots of both phases were reserved for analysis as previously described. The aqueous ferric iron concentration was deduced from Fig. 2. Ethereal ferric iron concentration was determined either by permanganate titration after zinc reduction or by the o-phenanthroline colorimetric method. Ferrous chloride has negligible solubility in the ether phase and was not determined.

As should be the case if equilibrium is established between the two phases, the e.m.f.'s of the ether phase cell agreed with those of the aqueous phase; the uncertainty in the measurements was less than 1 mv. The ether cells were somewhat erratic within this range, but became stabler when stirring was vigorous. Slight oxidation causes relatively

large changes in the ethereal ferrous iron concentration, with corresponding fluctuations in cell e.m.f. Vigorous agitation tended to keep the ferrous concentration near to the solubility limit.

TABLE I

E.M.F. Data for Distribution of Ferric Chloride Between $5^\circ F$ Hydrochloric Acid and Isopropyl Ether, Saturated with $FeCl_2 \cdot 4H_2O$ at $25.0 \pm 0.1^\circ$

	E.m.f. (mv.)			FeIII (Formula wt./liter)		
HCl$_{aq.}$	Aq.	Heavy	Light	Aq. X10^{-4}	Heavy	Light
	−347.7			0.797		0.00140^a
	−349.2			0.845		.00219^a
	−368.1			1.77		.00400^a
	−373.3			2.17		.00442^a
	−379.8			2.78		.00963^a
4.926	−385.5		−385.1	3.48		.04394
4.970	−387.1		−387.4	3.73		.08440
4.937	−389			3.99	0.3168	.1059
4.945	−389.1	−388.1		4.02	.3211	(0.1304)^b
5.015	−389.2	−389.1		4.04	.3758	
5.075	−388.8	−389.9		3.95	.3735	
5.042	−392.9	−392.5		4.65	.5170	
5.061	−399.8	−399.2		6.10	.5993	
4.955	−412.2	−411.8		9.95	.7734	

^{a} By o-phenanthroline method. ^{b} Doubtful analysis.

For certain ranges of total ferric iron concentration at equilibrium aqueous acidities above 4.5 F the system splits into three liquid phases (vide infra). The two least dense phases are ether-rich, and have been designated in Table I as "heavy"
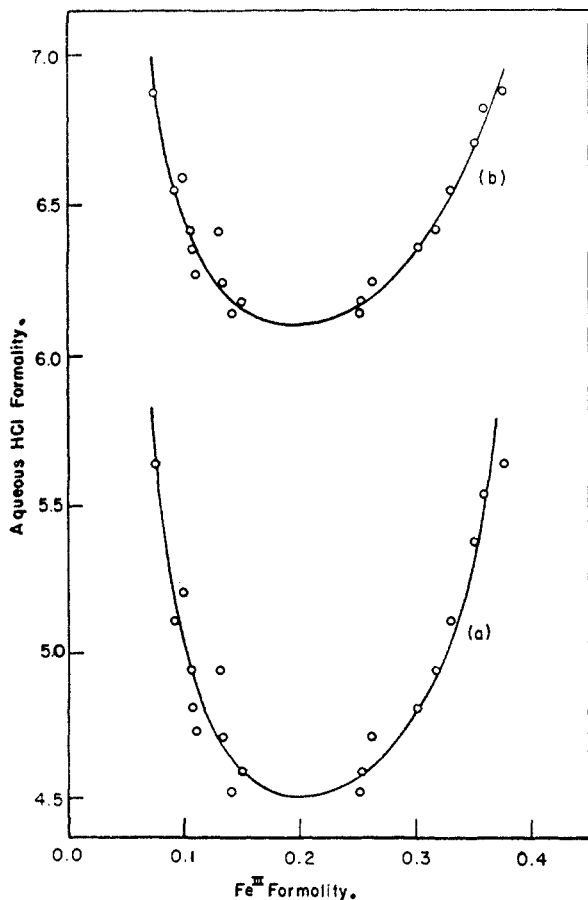

Fig. 7.—Ether immiscibility gap in presence of saturated $FeCl_2 \cdot 4H_2O$: (a) HCl = "free acid" (aqueous phase); (b) HCl = $\sqrt{(H^+)(Cl^-)}$ (aqueous phase).

and "light." Table I includes e.m.f. data for some three-phase systems, although the phase volumes were seldom such as to permit separate e.m.f. measurements in both ether-rich phases in the same experiment. The comparatively high resistance of the ether electrolytes and the susceptibility of ethereal ferrous chloride to concentration changes resulting from oxidation impose practical limitations on the direct determination of ethereal ferric chloride activity coefficients. The measurements do establish the existence of equilibrium, however, and confirm the conclusion that the cause of the anomalous extraction of ferric chloride is the remarkable decrease in the activity coefficient of that component with increasing concentration.

The Three-liquid Phase System

The appearance of a third liquid phase for certain ranges of ferric chloride and hydrochloric acid concentrations was first reported by Dodson, Forney and Swift.[12] Additional observations have been made by Myers and Metzler.[13] The authors have noted the existence of a three-liquid phase region in the system: gallium chloride, hydrogen chloride, isopropyl ether, water,[14] and unpublished results[15] from this Laboratory show the same behavior for the analogous auric chloride system.

The abnormally low activity coefficients of ferric chloride in the ether phase suggest an explanation for the separation of a third phase. As Fig. 6 shows, the activity coefficient of ethereal ferric chloride decreases with increasing concentration. At some critical concentration the activity of this component reaches a constant limiting value. Further increase in the ferric chloride concentration cannot increase the activity and the other phase splits into two phases of equal activity but different concentration. The system then becomes invariant at constant temperature and acidity, according to the phase rule.[16] As more ferric chloride
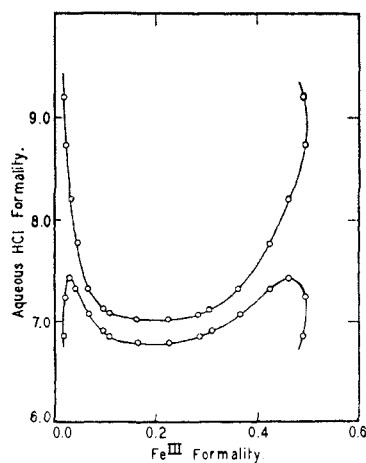

Fig. 8.

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

(13) R. J. Myers and D. E. Metzler, ref. 5.

(14) N. H. Nachtrieb and R. E. Fryxell, This Journal, **71**, 4035 (1949).

(15) C. G. Haas, Ph.D. Dissertation, The University of Chicago, 1950.

(16) The same argument applies to the five component system, since the concentration of ferrous chloride is fixed at saturation.
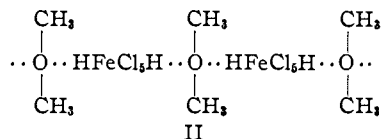
is added to the system the composition of each phase remains unaltered, but the relative phase volumes change. Ultimately one of the phases disappears and the system again becomes monovariant at constant temperature and acidity. The three-liquid phase region is indicated by the vertical dotted line of Fig. 5. Systems having average ethereal iron concentrations within this region split into two ether-rich phases of terminal composition. The appearance of a third phase is thus seen to be a consequence of the activity effects which operate in the ether, and is merely an extreme manifestation of the extraction anomaly observed in the two phase region.

The immiscibility gap for the two ether-rich phases of the three phase system has been determined for both the four and five component systems, as shown in Figs. 7 and 8. The effect of $FeCl_2 \cdot 4H_2O$ is to diminish the consolute acid concentration from 7.0 to 4.5 F. Presumably, this is due to an increase in the activity of hydrogen chloride by the addition of chloride ion.

A detailed explanation of the distribution anomaly or the three phase system is not provided by thermodynamics, and would require structural evidence. It is not unreasonable to suppose, however, that the normal extraction is a kind of generalized acid–base reaction in which hydrogen bonding links the chloroferric acid to the ether oxygen to form an "onium" salt (I).

$$\begin{array}{c} CH_3 \\ | \\ O \cdots HFeCl_4 \\ | \\ CH_3 \\ \\ I \end{array}$$
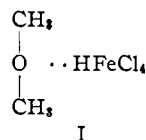
Deviations from normal extraction may be due to polymers, as Swift has suggested. Conceivably, chains might be formed by multiple hydrogen bonding (II).

$$\begin{array}{ccc} CH_3 & CH_3 & CH_3 \\ | & | & | \\ \cdots O \cdots HFeCl_5H \cdots O \cdots HFeCl_5H \cdots O \cdots \\ | & | & | \\ CH_3 & CH_3 & CH_3 \\ & II & \end{array}$$

Although empirical formulas have been determined for which the HCl : $FeCl_3$ ratio is as large as 4 large deviations from normal extraction occur when the ratio is still unity. It therefore appears that no such well-ordered structures exist as are implied by the term "polymerization," and the deviations from ideal behavior may be due to strong dipole interactions between ether molecules and chloroferric acid which produce "clusters" of indefinite size and structure.
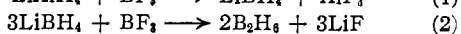

Preparation of Diborane by the Lithium Aluminum Hydride–Boron Trifluoride Reaction[1]

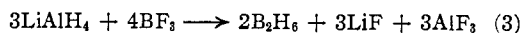BY I. SHAPIRO, H. G. WEISS, M. SCHMICH, SOL SKOLNIK AND G. B. L. SMITH

A study of the preparation of diborane by the reaction of lithium aluminum hydride and boron trifluoride etherate in ether reveals that there are at least two separate reactions involved in the process. First, the reactants in equimolar quantities form lithium borohydride and aluminum fluoride, and then the lithium borohydride reacts with additional boron trifluoride in a 3:1 molar ratio to give diborane and lithium fluoride. Under certain conditions a part of the lithium ends as lithium fluoborate, and the point at which it begins to form assists the interpretation of the whole process.

Of the various methods of producing diborane by the reaction of a boron trihalide with an active hydride,[2,3] one of the most convenient is the one in which solutions of lithium aluminum hydride and boron trifluoride in ether are brought together.[4] However, the yield of diborane is often not so nearly quantitative as might be expected, and the stoichiometry of the other products usually is not simple. As a step toward realizing maximum yields, the chemistry of the reaction has been studied in some detail.

By adding incremental amounts of boron trifluoride to lithium aluminum hydride, one finds that two successive reactions are the main steps in the generation of diborane. These can be expressed by the equations[5]

$$LiAlH_4 + BF_3 \longrightarrow LiBH_4 + AlF_3 \qquad (1)$$
$$3LiBH_4 + BF_3 \longrightarrow 2B_2H_6 + 3LiF \qquad (2)$$

or in sum

$$3LiAlH_4 + 4BF_3 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3 \quad (3)$$

as in the case of boron trichloride.[2] For the reverse order of addition of reactants Eq. 1 and 2 occur concurrently and, consequently, diborane is obtained immediately.

In any actual experiment, however, there usually is found a small proportion of lithium fluoborate, and sometimes a fluoaluminate complex salt, both of which are indicated by X-ray studies of the solid products. It would be reasonable to suppose that lithium fluoborate is formed during the reaction, and acts as a source of boron for the hydridation whenever or wherever the etherate of boron trifluoride is not present in local excess. This idea gains support from an experiment in which a suspension of lithium fluoborate in a solution (in ether) of lithium aluminum hydride was found to yield diborane quite readily.

ported here. For simplicity in writing the equations, the ether formula will be omitted.

(1) Published by permission of the Technical Director, U. S. Naval Ordnance Test Sta.

(2) A. E. Finholt, A. C. Bond and H. I. Schlesinger, THIS JOURNAL, **69**, 1199 (1947).

(3) D. T. Hurd, *ibid.*, **71**, 20 (1949).

(4) R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951); E. Nielsen, unpublished report.

(5) Boron trifluoride is present as the etherate in all reactions re-