The Extraction of Ferric Chloride into Non-aqueous Solvents.*
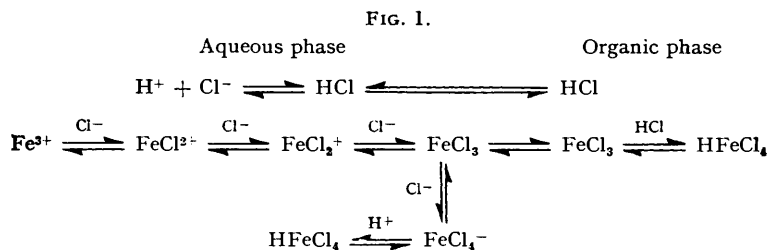
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The distributions of hydrochloric and hydrobromic acids between water and diethyl and di*iso*propyl ethers have been studied. Both phases have been analysed for acid, and the ether phase for water content. The distribution of ferric ions in the hydrochloric acid–ether–water systems has also been re-examined. The addition of methanol to the two-component, two-phase system of ethyl ether and aqueous hydrochloric acid affects the distribution of hydrochloric acid and ferric ions in a relatable fashion. Suggestions are made about the mechanism of these and similar extractions.

On the addition of hydrochloric acid to an aqueous ferric salt solution the amounts of the various possible ferric chloride complexes formed depend upon the final concentrations of the ions in solution in accordance with recently determined equilibrium constants (Gamlen and Jordan, *J.*, 1953, 1435). Over a limited range of acid concentration a complex, $FeCl_4H,wH_2O$, where w may well be as large as 10, can be extracted into ethers from the aqueous phase (Nachtrieb and Conway, *J. Amer. Chem. Soc.*, 1948, **70**, 3547, 3552; Myers, Metzler, and Swift, *ibid.*, 1950, **72**, 3767; Friedman, *ibid.*, 1952, **74**, 5). The simplest consideration of such an extraction must include the equilibria represented in Fig. 1. Similar equilibria will be set up for other metal halides which are extractable into ethers, *e.g.*, $InBr_3$ (Part III). The derivation of equations which should describe all such extractions has been given (Part I). In this paper experimental evidence on the extraction of ferric chloride into several non-aqueous solvents will be discussed. In the first instance, however, the extraction of the simple halogen acid must be described.

Fig. 1.

Aqueous phase   Organic phase

$H^+ + Cl^- \rightleftharpoons HCl \longleftarrow HCl$

$Fe^{3+} \overset{Cl^-}{\rightleftharpoons} FeCl^{2+} \overset{Cl^-}{\rightleftharpoons} FeCl_2^+ \overset{Cl^-}{\rightleftharpoons} FeCl_3 \rightleftharpoons FeCl_3 \overset{HCl}{\rightleftharpoons} HFeCl_4$

$HFeCl_4 \overset{H^+}{\underset{}{\rightleftharpoons}} FeCl_4^-$ (with Cl^-)

Extraction of Halogen Acids by Ethyl and iso*Propyl Ethers.*—From solutions of high molarity, >3M, hydrochloric and hydrobromic acids are extracted into the two ethers in amounts determinable by direct titration. Below this molarity, indirect methods of determination must be used. We have employed simple conductivity determinations in water of the organic-phase acid recovered by a back-extraction from the ether (p. 1926). Table 1 gives the results of the measurements for the extraction of the two acids into the two ethers when equal *initial* phase volumes are used. On the whole, our findings agree with the scattered data in the literature (Bock, Kusche, and Bock, *Z. analyt. Chem.*, 1953, **138**, 167). Although the phase changes on mixing are approximately constant over the range of acidities studied, there is always an increase in volume of about 5% in the aqueous phase.

In Part I it was shown that the distribution coefficient, q, of an acid should be given by

$$\partial \log q / \partial \log C_{HL} = \bar{\bar{h}} - \bar{h} \qquad \qquad (1)$$

where C_{HL} is the total acid in the system and $\bar{\bar{h}}$ and $\bar{h}$ are the average number of hydrogens bound per ligand atom, L, in the organic and the aqueous phase respectively. This

equation assumes that activities are constant, which is not true here. Now, from Table 1, virtually all the acid remains in the aqueous phase, so that C_{HL} is given by the concentration of the aqueous acid. Equation (1) can therefore be written

$$\partial \log q / \partial \log a_{HCl} = \bar{h} - \bar{\bar{h}}$$

where a_{HCl} is the activity of the aqueous acid.

TABLE 1. *Distribution of hydrochloric and hydrobromic acids between water and ethyl and isopropyl ethers.* [M = Molarity of aqueous acid initially.]

(A) Ethyl ether–water–hydrochloric acid; equal initial phase volumes.

M	1·72	1·95	2·16	2·40	2·60	2·82	3·04	4·88	5·17
log a_{HCl}	0·21	0·29	0·36	0·43	0·50	0·56	0·61	1·06	—
—log [HCl]$_{ether}$	3·70	3·60	3·55	3·50	3·40	3·28	3·25	2·80	2·65

(B) *iso*Propyl ether–water–hydrochloric acid; equal initial phase volumes.

M	2·16	2·60	2·82	3·24	3·47	4·36	4·88	5·42	6·00	8·00	10·00
log a_{HCl}	0·36	0·50	0·56	0·67	0·72	0·93	1·06	1·18	—	—	—
— log [HCl]$_{ether}$	4·00	3·85	3·67	3·60	3·40	3·04	2·66	2·40	2·10	1·70	1·00

(C) Ethyl ether–water–hydrobromic acid and (D) *iso*propyl ether–water–hydrobromic acid; equal initial phase volumes.

	(C)							(D)						
M	1·38	1·73	2·07	2·41	2·75	3·15	3·70	2·80	3·16	3·45	3·70	4·30	5·00	5·65
—log [HBr]$_{ether}$	4·00	3·80	3·58	3·40	3·28	3·17	2·91	4·00	3·92	3·82	3·70	3·45	3·30	3·20

Up to ~2·8M-acid, $\bar{h} - \bar{\bar{h}} = 0$ in both diethyl and di*iso*propyl ether extractions of hydrochloric acid, suggesting that hydrochloric acid is completely ionised in the ethers. No discussion of the extractions of hydrobromic acid can be made because of lack of activity data. In the extraction of hydrochloric acid the exponent $\bar{h} - \bar{\bar{h}}$ increases rapidly as the aqueous acidity increases above 3M. The results in other solvents (Part I) lead to the same observations. It should be noted that $\bar{h} - \bar{\bar{h}}$ may increase through changes in either the composition of the extracted species, " ideal " systems, or the partition coefficients, " non-ideal " systems. It is impossible to obtain satisfactory measurements on the extraction of hydriodic acid as it decomposes.

Variation of Water in the Organic Layer with Aqueous Acidity.—The equilibrium concentration of water extracted into *iso*propyl ether from aqueous hydrochloric acid has been shown to go through a minimum with increasing acid concentration (Campbell, Laurene, and Clark, *J. Amer. Chem. Soc.*, 1952, **74**, 6193). We have determined the concentration of water in ethyl ether equilibrated with an aqueous hydrochloric acid phase of different acid concentrations (see p. 1926) and the results are recorded in Table 2. Comparison between the results for the two ethers shows that the water in the ether layer varies in a parallel manner. However, the concentration of water in diethyl ether is always more than twice that in the *iso*propyl ether at the same acid concentration in the aqueous layer. Together with the phase volume changes this information shows that the respective ether layers

TABLE 2. *Extraction of water from aqueous hydrochloric acid into ethyl and isopropyl ethers.* (M = initial aqueous acid molarity.)

(A) Ethyl ether–water–hydrochloric acid : 5 ml. of aqueous solution shaken with 25 ml. of ether.

M	0·0	2·9	4·3	8·6	9·75	11·0	11·5
[H$_2$O]$_{ether}$	0·45	0·35	0·29	0·21	0·20	0·21	0·22

contain less water, whilst the aqueous phases in equilibrium with them contain more and more ether as the total acidity is increased. It is not to be expected therefore that the paritition coefficients of the acids, or their dissociation constants, will remain constant except at low acidities. Thus the distribution of metals in the systems must also be expected to be one of a " non-ideal " rather than of an " ideal " kind (cf. Part I). The distribution of acid and water is of importance in making this differentiation.

Effect of Methyl Alcohol on the Partition of Acid.—The extraction of metal halides can be

brought about by a wide variety of solvents which are only partially miscible with water. In general, it is observed that the more polar the organic solvent the more readily it extracts the halide (Part I). As an investigation of the effect of a number of different single solvents was being made (Part V), it was decided to adjust the extracting power of one solvent, ethyl ether, by adding different amounts of a third component, methanol. Such three-component solvent systems are often employed in inorganic chromatography, especially on cellulose supports. We have discussed such matters elsewhere (Chalkley and Williams, *J.*, 1954, 1718).

First, the changes in distribution of both water and hydrochloric acid between the two phases were examined over a wide acidity range. Table 3 illustrates the differences in

TABLE 3.

M		0·0	1·1	2·2	4·2	7·8	9·6	11·5
A	Volume of lighter phase	25·0	24·8	24·4	23·7	20·7	18·0	15·4
	Volume of heavier phase	5·0	5·2	5·7	6·6	10·0	12·7	14·6
B	Volume of lighter phase	30·1	24·5	21·4	19·4	17·2	—	15·7
	Volume of heavier phase	6·1	12·1	14·9	17·0	19·6	—	21·6

final phase volumes at different acidities for the initial solvent systems : (A) 25 ml. of ether and 5 ml. of aqueous acid; (B) as (A) but with addition of 7·5 ml. of methanol. The data show that the phase volume changes on mixing are much larger in the system containing methanol if conditions of equal acidity are compared. Increasing miscibility of the phase will generally lead to departures from " ideal " behaviour at lower acidities and be accompanied by large volume changes. Measurements of the equilibrium water content of the lighter phase are given (Table 4) for the solvent system including methanol, system (B).

TABLE 4.

Initial [HCl] molarity ...	0·0	0·1	0·6	1·15	2·15	2·88	4·30	8·63	11·5
Final [H$_2$O] molarity...	8·9	7·4	3·9	3·3	2·5	1·9	1·3	0·3	0·23

These results can be compared directly with those given in Table 3. It seems likely that the loss of water from the lighter phases is due to the solvation of the increasing amount of acid in the aqueous phase.

We have also studied the changes in acid normality in both the aqueous and the organic phase at equilibrium as the amounts of acid and the amounts of methanol in the phases have been separately varied. In every case the final acid normality in the aqueous phase increases almost linearly with increasing total acid but the final molarity in the lighter phase undergoes much more irregular changes (Fig. 2 and Table 5). The appearance

TABLE 5. *Distribution of hydrochloric acid between the two phases formed from different mixtures of methanol, ethyl ether, and water* (Fig. 2).

In each system 25 ml. of ether, 5·0 ml. of water, and V ml. of methanol were taken. The initial acid concentration (M) is that in the water added; N_0 and N give the final acid normalities in the organic and aqueous layers, respectively.

V =	0·0		5·5		7·5		8·0	
M	N_0	N	N_0	N	N_0	N	N_0	N
1·12	0·0	1·11	0·004	0·72	0·031	0·38	—	—
1·84	—	—	—	—	—	—	0·084	0·50
2·20	0·0	1·96	0·007	1·05	0·045	0·69	—	—
2·46	—	—	—	—	—	—	0·090	0·57
4·25	0·001	3·65	0·010	1·73	0·042	1·33	—	—
5·56	—	—	—	—	—	—	0·042	1·40
6·12	0·006	4·40	0·010	2·31	—	—	—	—
7·90	0·015	4·45	—	—	0·022	—	0·033	2·05
11·45	0·085	4·75	0·025	3·78	0·032	3·25	0·033	3·05

of maxima in the acid concentration in the organic phase must be a consequence of the falling water and methanol concentration in this layer which undergoes large changes in composition. In order to show how the final water and acid concentrations in the lighter

phase were related, when different amounts of methanol were added, we measured the water content of the light phases resulting from the equilibration of 25 ml. of ether, 5·0 ml. of aqueous hydrochloric acid (2·78M), and different volumes V of methanol. The results are recorded in Table 6. The two concentrations are seen to be closely related.

TABLE 6.

V, ml.	0	2·5	5·0	6·5	7·5	7·7	8·0
Final [HCl] in light phase	0·0	0·003	0·008	0·025	0·043	0·06	0·07
Final [H$_2$O] in light phase	0·35	0·60	1·00	1·37	2·20	3·41	4·34

Extraction of Ferric Chloride into Diethyl and Diisopropyl Ether.—In Fig. 1 a set of equilibria has been given which, as stated, should be suitable for a description of ferric chloride extractions. In the Figure there are no equilibria relating to the formation of

FIG. 2. *The distribution of hydrochloric acid between aqueous and organic layers, using the initial solvent systems shown.*
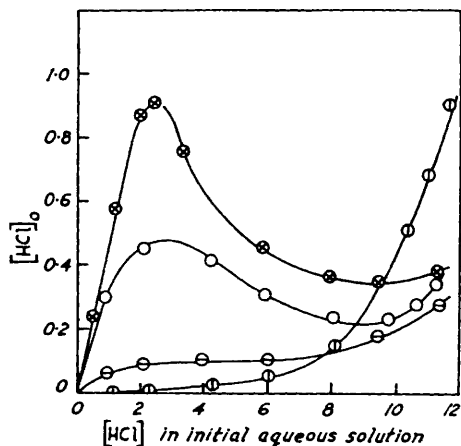
5 ml. of aqueous acid plus ⊕ 25 ml. of ethyl ether; ⊖ 25 ml. of ethyl ether + 5 ml. of methanol; ○ 25 ml. of ethyl ether + 7·5 ml. of methanol; ⊗ 25 ml. of ethyl ether + 8 ml. of methanol.

The intersection of the curves is a result of plotting the equilibrium organic acid concentration against the initial aqueous acid concentration and would disappear if the equilibrium acid concentration in the heavier phase were plotted for the latter.

FIG. 3. *The variation of extraction of iron (ferric),* log q_{Fe}, *with concentration of hydrochloric acid in the organic layer,* — log [HCl]$_o$, *in the solvent systems shown.*
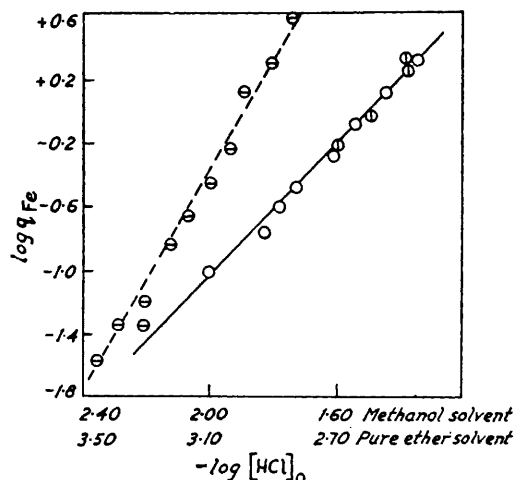
⊖ 25 ml. of aqueous acid, 25 ml. of ethyl ether; ⊕○ 5 ml. of aqueous acid, 25 ml. of ethyl ether, 7·5 ml. of methanol.

The points marked ○ represent increasing acid and iron extraction with increasing total acidity and those marked ⊕ decreasing acid and iron extraction with increasing total acidity.

polynuclear complexes (cf. Part IV, and Herber, Bennett, Bentz, Bogar, Dietz, Golden, and Irvine, Abs. 126th Meeting, Amer. Chem. Soc., 1954, p. 33R). We dismissed the necessity for considering such species for the following reasons. (*a*) The spectra of ferric chloride in ether extracts from aqueous hydrochloric acid, in ethanol solutions in the presence of lithium chloride, in methanol in the presence of hydrochloric acid, in water in concentrated hydrochloric acid, and in solid compounds of formula $M^I FeCl_4$, where M^I is an alkali-metal cation, are all identical (Friedman, *loc. cit.*). (*b*) Analyses of ether extracts of ferric chloride from aqueous hydrochloric acid give the formula $HFeCl_4$ (p. 1920). (*c*) A Beer's law plot of the absorption of the extracts in the ether solvents is linear over the range from 10^{-3} to $1·0$M. (*d*) The extraction of ferric chloride into *iso*propyl ether is independent of iron concentration over the range 10^{-5} to $10^{-2·5}$M-iron at low acidities. At high acidities the extraction conditions are suspected of being "non-ideal" (p. 1921), so that large deviations are to be expected from causes other than polymerisation. In this paper

therefore it will be assumed that polymerisation is absent at low iron concentrations and acidities.

The results we have obtained on the extraction of ferric chloride into diethyl ether are given in Table 7. The total iron concentration used was $\ll 10^{-3}$M. This extraction being considered to be " ideal " the following equation holds (Part I) :

$$\partial \log q/\partial \log C_{HL} = (\bar{\mathbf{h}} - \bar{h}) + (\bar{\mathbf{n}} - \bar{n}) \quad \ldots \quad \ldots \quad (2)$$

where q is the distribution coefficient of iron, and $\bar{\mathbf{h}}$, $\bar{h}$, $\bar{\mathbf{n}}$, and $\bar{n}$ refer to the degree of formation of the complexes in the two phases, the complexes in the water phase being assumed to be represented by $H_{\bar{h}}FeCl_{\bar{n}}$ and in the organic phase by $H_{\bar{\mathbf{h}}}FeCl_{\bar{\mathbf{n}}}$. Gamlen and Jordan (*loc. cit.*) have shown that in 2·0M-hydrochloric acid $\bar{n} \sim 2·5$, and in 5·0M-acid $\bar{n} \sim 3·0$. Assuming that $\bar{h} \sim 0$ and knowing the formula of the extracted complex to be $H_{1·0}FeCl_{4·0}$, we can reduce equation (2) to $\partial \log q/\partial \log C_{HL} = 2·5 \longleftrightarrow 2·0$. Now as total acid is equal to the acid in the aqueous layer to a first approximation this equation can be expressed as $2·0 \longleftrightarrow 2·5 = \partial \log q/\partial \log a_{HCl}$ where a_{HCl} is the activity of the acid in the aqueous phase. The results show that the slope is much greater than this figure and the system is apparently " non-ideal."

TABLE 7. *The extraction of ferric ions into diethyl ether at different hydrochloric acid normalities.*

Equal volumes of ether and aqueous acid. Final volume of aqueous phase, 22·3 ml.; final volume of organic phase, 27·5 ml. Total iron, added in aqueous phase, 10^{-3}M.

Aqueous acid concn.					Aqueous acid concn.				
Initl	Final	$\log q_{Fe}$	$-\log [\mathrm{HCl}]_{ether}$	$\log a_{HCl}$	Initl.	Final	$\log q_{Fe}$	$-\log [\mathrm{HCl}]_{ether}$	$\log a_{HCl}$
2·46	2·20	−1·60	3·44	0·40	3·58	3·22	−0·50	3·10	0·66
2·69	2·50	−1·38	3·37	0·46	3·81	3·41	−0·24	3·04	0·71
2·91	2·66	−1·19	3·30	0·52	4·03	3·59	0·10	2·99	0·75
3·13	2·86	−0·86	3·23	0·56	4·26	3·74	0·27	2·92	0·80
3·36	3·06	−0·70	3·17	0·62	4·47	3·93	0·64	2·85	0·84

The extraction of ferric chloride into *iso*propyl ether has been extensively studied (Nachtrieb and Conway, *loc. cit.*). Using Gamlen and Jordan's data we can again calculate the differences in the degree of formation of the complexes in the two phases over the range of acidities where distribution can be studied. Equation (3) then becomes $\partial \log q/\partial \log a_{HCl} \approx 2·0$. The experimental results again give a much higher value of this function (Table 8). It appears safe to conclude that the sequential equilibria

TABLE 8.

Initial acid concn.	3·0	4·0	4·5	5·0	6·0
$\log a_{HCl}$	0·58	0·85	0·97	1·08	1·29
$\log q_{Fe}$	−2·60	−1·40	−0·83	−0·42	0·60

involved in Fig. 1, polymerisation (which is excluded on other grounds) being omitted, cannot alone account for the results. Changes in solvent activity must be considered.

Distribution of Ferric Chloride in Systems containing Methanol.—The distribution of hydrochloric acid in several of the three-component two-phase systems described in Table 5 goes through a maximum with increasing acid. The distribution of ferric chloride into such solvents was now studied in order to determine whether similar maxima appeared in its extraction. The solvent chosen for such a test was that given by 25 ml. of ethyl ether, 7·5 ml. of methyl alcohol, and 5 ml. of aqueous acid of different concentrations. It was first shown that the distribution coefficient of iron was independent of concentration below 0·002M-Fe. The iron distribution at the different acidities is given in Table 9, and a plot of $\log q_{Fe}$ against $\log [\mathrm{HCl}]_o$ in Fig. 3. The iron extraction goes through a maximum when $[\mathrm{HCl}]_o$ is a maximum. The logarithmic plot reveals that the values of $\log q$ on either side of the maximum lie on the same straight line, except at initial acidities greater than 8M.

Similar distribution maxima have been observed in the extraction of certain actinide and lanthanide complexes (Peppard, Gray, and Markus, *J. Amer. Chem. Soc.*, 1953, **75**, 6063; Peppard, Foris, Gray, and Mason, *J. Phys. Chem.*, 1953, **57**, 294).

Our first attempt to explain this behaviour assumed an equilibrium in the organic phase between acid and ferric chloride: $FeCl_3 + HCl \rightleftharpoons FeCl_4H$, implying (Fig. 1) that more than one species was extracted. This is readily tested by measurement of the absorption spectrum of the extracted iron solutions at different acidities. The spectra obtained at acidities of 0·56, 1·20, and 5·65M-hydrochloric acid, *i.e.*, on both sides of the

TABLE 9. *Extraction of ferric ions from methanol-containing solvent systems.*

Solvent: 25 ml. of ether, 5 ml. of aqueous hydrochloric acid, of normality N, 7·5 ml. of methyl alcohol. Initial aqueous iron = 10^{-3}M.

N	0·122	0·232	0·329	0·378	0·458	0·572	0·680
$-\log [HCl]_{organic}$	2·25	1·99	1·85	1·77	1·73	1·59	1·55
$\log q_{Fe}$	−1·36	−1·04	−0·77	−0·64	−0·48	−0·29	−0·09
N	1·120	2·200	3·24	4·25	5·80	6·18	
$-\log [HCl]_{organic}$	1·45	1·35	1·39	1·38	1·50	1·61	
$\log q_{Fe}$	0·10	0·28	0·27	0·24	−0·06	−0·21	

maximum distribution, were identical even in so far that the extinction coefficients at maximum absorption varied insignificantly. Further, the relative absorption at different wavelengths was that to be expected for $FeCl_4^-$ (Friedman, *loc. cit.*). Thus only one spectroscopically distinct species is extracted. A second equilibrium in the organic phase which could control distribution is $FeCl_4^- + H^+ \rightleftharpoons HFeCl_4$. This equation, however, gives the wrong dependence of iron distribution upon acid concentration in the organic phase, for it is found that the former varies as $[HCl]_o^2$. The third possibility is that the distribution is partly dependent on equilibria such as those given and partly on change in partition coefficient due to changes in the activities of the solvent. The latter would account for the changing distribution of the hydrochloric acid as well as of the ferric chloride, for it has been shown that the former is dependent on the concentration of water in the organic phase (p. 1923). In this connection it is noteworthy that, at the acidities where the extraction of ferric chloride into the ethers begins to increase rapidly, the extraction of the acid also rises sharply.

A further test of the effect of solvent changes was now made. Ferric chloride was extracted into the solvent system formed from the three components, methanol (*V* ml.), ethyl ether (25 ml.), 2·78M-hydrochloric acid (5 ml.). As *V* is increased the system passes very close to the plait-point of the methanol–acid–ether system beyond which only one phase remains. The data are given in Table 10. As the amount of methanol is increased, the acidity of the aqueous phase falls and that of the organic phase increases, both approaching 0·2—0·4M. At the same time the distribution coefficient of water also

TABLE 10. *Extraction systems containing a varying amount of methanol but a constant amount of acid* [5·0 ml. of aqueous acid (2·78M); 25 ml. of ethyl ether; *V* ml. of methanol].

	Final acidity :		Final $[H_2O]$:	
V	lighter phase	heavier phase	lighter phase	q_{Fe}
0·0	—	2·40	0·35	0·06
2·5	0·0032	1·71	0·60	0·60
5·0	0·0085	1·25	1·00	2·11
6·5	0·0252	0·99	1·37	2·35
7·5	0·043	0·85	2·20	1·94
8·0	0·070	0·73	4·34	1·71
8·5	0·098	0·66	5·80	1·47
9·0	0·12	0·53	—	1·32

approaches unity. At the plait-point the distribution coefficients of all the species in the system must be unity (Part I). The manner in which the distribution coefficient for iron approaches this value is that it first increases to a value greater than unity and then falls towards unity. This maximum in distribution cannot be due to sequential equilibria, as

the ligand concentration in the aqueous phase is falling. The variations in distribution are due to " non-ideal " behaviour, *i.e.*, to changes in the activities of the solvents in the two phases.

Maxima in distribution coefficients have been observed in many other systems in circumstances which are not controlled by sequential equilibria. In particular, the experimental observations by Irving and Rossotti (*Analyst*, 1952, **77**, 801) do not lend themselves to such an interpretation. The fact that the metal involved is independent of the variation of distribution with acidity at higher acidities can only be explained in terms of changing partition coefficients, *i.e.*, non-ideal extraction conditions. However, in other cases unexpected changes in distribution with change of metal-ion concentration have been interpreted as arising from polymerisation in the aqueous phase (Herber *et al.*, *loc. cit.*; and see Part IV). In the authors' view it seems more probable that such depressions of extraction with rising cation concentration arise from the changing activity of the solvents (cf. MacKay, *Trans. Faraday Soc.*, 1952, **48**, 1103).

Experimental.—The concentration of acid in the organic phase in equilibrium with different aqueous acid concentrations was determined as follows : 25 ml. of aqueous acid were shaken with the same volume of organic solvent in a stoppered glass tube. Equilibrium was shown to be established in 10 min.; 10 ml. of the organic phase were then pipetted into a second tube containing 10 ml. of distilled water. After 10 minutes' shaking, effectively all the acid had been extracted into the aqueous layer; the partition coefficient of hydrochloric and hydrobromic acids is about 10^4, favouring the aqueous phase. As there was no measurable volume change during the second operation, the concentration of acid in the original organic layer was now given by that in the aqueous layer. The latter concentration was found by determining the conductivity by use of a probe-type conductivity cell of the usual simple design. The conductivity of acid corresponding to a given conductivity was then read off on a previously prepared calibration graph. The conductivity of the distilled water used was lower by a factor of ten than any of the readings used in compiling Table 1.

Conductivity of the ether layer. The ether layer was shown to have a well-defined conductivity after equilibration with aqueous hydrochloric acid by simple experiments using the conductivity cell and bridge as in the above experiments. It was suspected that the conductivity observed might be due, at least in part, to a layer of moisture on the glass supports of the platinum wires forming the conductivity cell. This was disproved by showing that the measured conductivity of the ether layer was dependent on the extent to which the wire electrodes were immersed in the ether. The conductivity was not directly proportional to the amount of acid in the ether, and we attribute the lack of correlation between these two qualities to the incomplete dissociation of the acid in the ether. It was for this reason that the acid in the ether layer was determined by the back-extraction described above.

Determination of ferric iron concentrations. Ferric concentrations were determined by the thiocyanate method. The details of our procedure followed those recommended by Sandell (" Colorimetric Analysis for Trace Metals," Interscience, New York, 1950, p. 363).

Determination of water content of ether layer. The usual Karl Fischer method was employed. Our technique differed only in a few minor respects from that of Smith, Bryant, and Mitchell (*J. Amer. Chem. Soc.*, 1939, **61**, 2407) and we prepared our reagents by their methods.