295. *A Spectrophotometric Study of the Iron*(III) *Chloro-complexes.*

By G. A. Gamlen and D. O. Jordan.

The nature of the chloro-complexes of iron(III) in concentrated hydrochloric acid solution is discussed, and from a consideration of previous data and some new results it is concluded that the highest chloro-complex formed has the formula $FeCl_4^-$.

Values of the third and fourth association constants are obtained together with values of $\varepsilon_{FeCl_4^-}$, ε_{FeCl_3}, and $\varepsilon_{FeCl_2^+}$ at wave-lengths in the range 220—440 mμ. The values of the extinction coefficient in the range 400—440 mμ are in agreement with values given previously even though the calculations are based on different assumptions.

The association of the Fe^{3+} ion with chloride ions in solutions of hydrochloric acid may be represented, according to Bjerrum's theory of complex formation (Thesis, Copenhagen, 1941) and with neglect of the hydration of the metal and complex ions, as follows :

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+} \quad K_1 = a_{FeCl^{2+}}/a_{Fe^{3+}} \, . \, a_{Cl^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$FeCl^{2+} + Cl^- \rightleftharpoons FeCl_2^+ \quad K_2 = a_{FeCl_2^+}/a_{FeCl^{2+}} \, . \, a_{Cl^-} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$FeCl_2^+ + Cl^- \rightleftharpoons FeCl_3 \quad K_3 = a_{FeCl_3}/a_{FeCl_2^+} \, . \, a_{Cl^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$FeCl_3 + Cl^- \rightleftharpoons FeCl_4^- \quad K_4 = a_{FeCl_4^-}/a_{FeCl_3} \, . \, a_{Cl^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

These complexes have already been investigated both electrometrically and spectrophotometrically, but although considerable evidence has been accumulated concerning the nature of the highest complex and the values of K_1 and K_2, neither are there accurate data for K_3 and K_4 nor has the spectrum for each complex in the ultra-violet, which are of greater significance than the visible spectra, been recorded. Bent and French (*J. Amer. Chem. Soc.*, 1941, **63**, 568), using the $FeCNS^{2+}$ ion as a coloured indicator for the concentration of free Fe^{3+} ions, obtained a value for K_1, but owing to their neglect of the higher complexes and to the possible formation of mixed chloro- and thiocyanato-complexes, their result must be regarded as approximate. Rabinowitch and Stockmayer (*ibid.*, 1942, **64**, 335), from an extensive spectrophotometric study of the spectra of ferric perchlorate solutions containing hydrochloric acid, obtained values for K_1 and K_2 and gave an estimate of the value of K_3. They also obtained the spectra for the hydrated ferric ion, Fe^{3+} (aq.), and of the three species $FeCl^{2+}$, $FeCl_2^+$, and $FeCl_3$ over the range 400—460 mμ. A similar study, but in the ultra-violet region of the spectrum, was made by Olerup (Thesis, Lund, 1944; *Svensk Kem. Tidskr.*, 1943, **55**, 324), who also obtained values for K_1 and K_2 and an estimate of the value of K_3 for the complexes in $2M$-perchloric acid solution, which were in reasonable agreement with Rabinowitch and Stockmayer's results (*loc. cit.*).

The spectra of ferric chloride or perchlorate in solutions of various concentrations of hydrochloric acid have also been recorded by Ábrahám (*Acta Univ. Szeged*, 1938, *b*, **6**, 272), Kiss, Ábrahám, and Hegedüs (*Z. anorg. Chem.*, 1940, **244**, 98). and Metzler and Myers (*J. Amer. Chem. Soc.*, 1950, **72**, 3776), but no attempt was made by these authors to obtain either the association constants or the spectra of the individual ionic species existing in solution.

In this communication we describe the determination of the association constants K_3 and K_4 and of the spectra of $FeCl_2^+$, $FeCl_3$, and $FeCl_4^-$. These results, taken with those of Rabinowitch and Stockmayer (*loc. cit.*) and of Olerup (*loc. cit.*), thus completely describe the nature of the chloro-complexes of the ferric ion in solution.

Theoretical Discussion.—Solutions of ferric chloride in water contain, in addition to the chloro-complexes, the hydroxy-complexes $Fe(OH)^{2+}$, $Fe(OH)_2^+$, and $Fe(OH)_3$ which have already been extensively investigated (Lamb and Jacques, *J. Amer. Chem. Soc.*, 1938, **60**, 967, 1215; Rabinowitch and Stockmayer, *loc. cit.*; Bray and Hershey, *J. Amer. Chem. Soc.*, 1934, **56**, 1889; Brosset, *Svensk Kem. Tidskr.*, 1941, **53**, 434; Olson and Simonson *J. Chem. Phys.*, 1949, **17**, 1322; Siddall and Vosburgh, *J. Amer. Chem. Soc.*, 1951, **73**, 4270). According to Rabinowitch and Stockmayer (*loc. cit.*) the absorption by the hydroxy-complexes is sufficiently large to interfere with the spectra of the chloro-complexes even when the former are present in very small quantities. It is therefore necessary to employ a strong non-complexing acid medium when the lower chloro-complexes are studied in order to prevent the formation of the hydroxy-complexes, and perchloric acid is generally used for this purpose (see Rabinowitch and Stockmayer, *loc. cit.*). Recently, Sutton (*Nature*, 1952, **169**, 71) has shown that a ferric ion–perchlorate ion pair is formed in solutions of 10^{-4}M-ferric perchlorate in perchloric acid of concentration between 1 and 7M. The value of the constant (K_p) for the association

$$Fe^{3+} + ClO_4^- \rightleftharpoons FeClO_4^{2+}$$

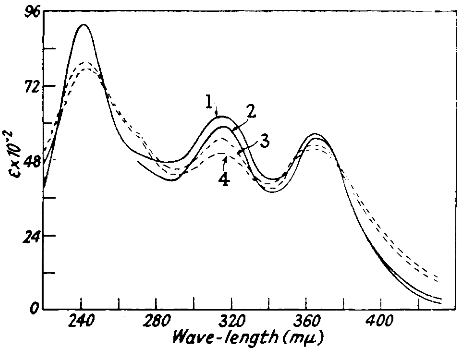
is, however, so small compared with the values of K_1 that have been recorded that the latter values are unlikely to be in serious error owing to the ion-pair formation [$K_1 = 30$ (Rabinowitch and Stockmayer, *loc. cit.*), $K_p = 0{\cdot}47$ (Sutton, *loc. cit.*)].

Formula of the highest chloro-complex. Direct evidence for the nature of the highest complex formed is not easy to obtain, but information can be obtained from experiments in which the aqueous solution is extracted with a suitable organic solvent, and the nature of the extracted species determined by direct analysis. Comparison can also be made between the absorption spectra of the extract and of the original aqueous solution. Using these methods, Nachtrieb and Conway (*J. Amer. Chem. Soc.*, 1948, **70**, 3547) showed that the chloro-complex extracted from solutions containing 2—8M-hydrochloric acid has the formula $HFeCl_4$, and that at concentrations above 8M, the molar ratio of HCl to $FeCl_3$ rises to 4. Nachtrieb and Conway were unable to decide whether this observation should be interpreted as evidence for the formation of higher complexes of formula H_2FeCl_5, H_3FeCl_6, etc., or as a salting-in effect caused by the $FeCl_3$. However, they point out that the ethereal extract of the solution of the complex in 7·5M-hydrochloric acid obeys Beer's law over the concentration range 0·01—0·4 mole/l. of iron at various wave-lengths in the visible region of the spectrum, which suggests the existence of only a single species in this solution. Furthermore, the spectrum of this extract is identical with that of extracts from solutions containing hydrochloric acid of concentration greater than 8M, in which up to 3 molecules of hydrochloric acid are associated with one molecule of ferric chloride. This evidence would appear to indicate that $HFeCl_4$ is the highest complex formed. This result has been confirmed by Myers, Metzler, and Swift (*J. Amer. Chem. Soc.*, 1950, **72**, 3767), who also showed that there is a great similarity between the spectra of the chloro-complexes present in aqueous solutions of concentrated hydrochloric acid (*ca.* 11·5M) and that of the complex extracted therefrom by *iso*propyl ether (see also Metzler and Myers, *loc. cit.*) and which was shown to have the formula $HFeCl_4$.

A spectrophotometric study of solutions of ferric perchlorate in ethyl alcohol containing lithium chloride (10^{-2} to 1M), taken in conjunction with the results of conductometric titration, led Brealey, Evans, and Uri (*Nature*, 1950 **166**, 959) to conclude that the ion $FeCl_4^-$ is formed quantitatively under these conditions and that no higher complex occurs. The spectrum of the chloro-complex under these conditions in ethyl alcohol is very similar to that obtained in aqueous solutions of hydrochloric acid at a concentration of 11·5M, as shown in Fig. 1, and it would therefore appear that the same complex predominates in both solvents. Brealey and Uri (*J. Chem. Phys.*, 1952, **20**, 257) have attempted to verify the formula $FeCl_4^-$ for the highest complex by plotting $\log\{[FeCl_4^-]/[FeCl_3]\}$, evaluated from their absorption spectra data on alcoholic solutions, against log [LiCl]. A straight line of slope approximately 1·4 was obtained, and Brealey and Uri attribute the deviation from the theoretical slope of unity to partial solvolysis of $FeCl_3$, an explanation which is equivalent to suggesting a difference in the co-ordination number of $FeCl_4^-$ and $FeCl_3$ (see below).

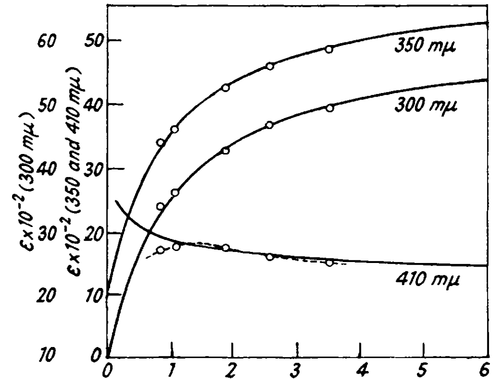
More positive evidence concerning the nature of the highest complex has been obtained by Friedman (*J. Amer. Chem. Soc.*, 1952, **74**, 5) who prepared salts of the type $M'M'''Cl_4$, where M′ is K^+, Cs^+, or NH_4^+ and M‴ is Fe^{3+} or Al^{3+}. The absorption spectra of the iron salts in the solid state and in solution in ethylene bromide and ethyl ether are very similar and closely resemble the spectra of ferric chloride in 11·5M-hydrochloric acid and of the ether extracts therefrom.

FIG. 1. *Absorption spectra of ferric chloride in solutions of high chloride-ion concentration.*



Full line: dry ethyl alcohol as solvent. Broken line: water as solvent. 1, 3·62M-LiCl; 2, 0·31M-LiCl; 3, LiCl–HCl *mixture, chloride-ion concentration* 12·5M; 4, 11·5M-HCl.

FIG. 2. *Variation of extinction coefficient with chloride ion activity at various wave-lengths.*



Open circles represent experimental points. Full curves are calculated from equation (13).

We have attempted the preparation of higher chloro-complexes than $FeCl_4^-$ in both alcoholic and aqueous solution. In view of the ease with which the $FeCl_4^-$ ion is formed in ethyl alcohol (Brealey, Evans, and Uri, *loc. cit.*), we studied the spectrum of ferric chloride solutions in ethyl alcohol saturated with lithium chloride (*ca.* 3M). At this concentration of chloride, which is 300 times that required for the almost quantitative formation of $FeCl_4^-$, the spectrum is identical in form with that at 0·1M-lithium chloride, which would appear strong evidence for the non-formation of a higher complex (Fig. 1). That the values of the extinction coefficient are slightly greater for the higher chloride concentrations is best explained on the basis of a shift in the equilibrium represented by equation (4) to favour the formation of $FeCl_4^-$.

The behaviour of aqueous solutions of ferric chloride is very similar. In very concentrated chloride solutions, obtained by saturating concentrated hydrochloric acid with lithium chloride, the spectrum of the chloro-complex remained almost identical with that obtained in the solution of concentrated hydrochloric acid alone (Fig. 1), there being a slight intensification of the characteristics of the $FeCl_4^-$ spectrum but a non-appearance of any new features. This result is a confirmation of the work of Friedman (*loc. cit.*), who obtained the spectrum of the chloro-complex existing in 16M-hydrochloric acid prepared by saturating the concentrated acid with hydrogen chloride under pressure. These results are again best explained by a small shift in the equilibrium favouring an increase in the concentration of $FeCl_4^-$ rather than by the formation of any new species.

Further support for the conclusion that the $FeCl_4^-$ ion is the limiting complex is given by the variation of the extinction coefficients with chloride activity. At all wave-lengths ε tends to a limiting value at the highest chloride-ion activity used (Fig. 2). It is unlikely that this would be so if a fifth complex were formed unless this complex had ε values close to those for $FeCl_4^-$, but in view of the relatively high ε values of $FeCl_4^-$ over the range 220—380 mμ it is probable that there would be at least one region of the spectrum in which the value of ε for the fifth complex was lower than for $FeCl_4^-$. At wave-lengths greater than 400 mμ there is a small maximum (see broken line in Fig. 2) in the value of ε at relatively low chloride-ion activities (*ca.* $1{\cdot}3 \times 10^2$) due to ε_{FeCl_3} being greater than $\varepsilon_{FeCl_4^-}$ at these wave-lengths. At high values of the chloride-ion activity, however, ε still tends to a limiting value.

There thus appears to be strong presumptive evidence that the $FeCl_4^-$ ion is the limiting chloro-complex of the ferric ion. This conclusion does not in itself indicate that the co-ordination number of iron in this complex is four and not six, but Friedman (*loc. cit.*) has shown that a change of solvent has very little effect on the spectrum of $KFeCl_4$, which suggests that there is no co-ordination of solvent molecules to the central atom and that the co-ordination number of iron in $FeCl_4^-$ is four. The change in co-ordination number of iron from six in Fe^{3+} and $FeCl^{2+}$ to four in $FeCl_4^-$ is in keeping with the generalisation (see, *e.g.*, Nyholm, *J.*, 1952, 1257) that metals having more than one co-ordination number show the maximum co-ordination number in cationic complexes and this decreases through non-ionic compounds to anionic complexes.

Determination of the association constants. The general form of the association equilibrium, activities being written in terms of concentrations and activity coefficients, is

$$K_n = \frac{[FeCl_n^{3-n}]}{[FeCl_{n-1}^{4-n}][Cl^-]} \cdot \frac{f_{FeCl_n^{3-n}}}{f_{FeCl_{n-1}^{4-n}} f_{Cl^-}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which the activity coefficients $f_{FeCl_n^{3-n}}$ and $f_{FeCl_{n-1}^{4-n}}$ are not known except for $FeCl_3$, which Nachtrieb and Fryxell (*J. Amer. Chem. Soc.*, 1952, **74**, 897) find to be approximately 1·0 at concentrations of $FeCl_3$ up to 0·1M in 5M-hydrochloric acid saturated with $FeCl_2,4H_2O$. An exact treatment without the introduction of non-thermodynamic assumptions is therefore not possible. The approximation generally made (see Bjerrum, *Kgl. Danske Videnskab. Selskab., Mat.-fys. Medd.*, 1946, **22**, No. 18; Näsänen, *Acta Chem. Scand.*, 1950, **4**, 140, 816) is to assume that a single mean activity coefficient, *F*, may be used to replace the activity coefficient term in equation (5), *i.e.*,

$$\frac{1}{F} = \frac{f_{FeCl^{2+}}}{f_{Fe^{3+}} f_{Cl^-}} = \frac{f_{FeCl_2^+}}{f_{FeCl^{2+}} f_{Cl^-}} = \frac{f_{FeCl_3}}{f_{FeCl_2^+} f_{Cl^-}} = \frac{f_{FeCl_4^-}}{f_{FeCl_3} f_{Cl^-}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This approximation is equivalent to assuming that

$$f_{FeCl_n^{3-n}}/f_{FeCl_{n-1}^{4-n}} = C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where *C* is a constant, *i.e.*, that the activity coefficients of the complexes change uniformly throughout the series. As Bjerrum (*loc. cit.*) points out, this is not an unreasonable assumption for solutions of high ionic strength for which chemical structure rather than charge determines the value of the activity coefficients.

Bjerrum (*loc. cit.*) then expresses *F* by the equation

$$\log F = A + B[Cl^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which *A* and *B* are constants for a particular system. This equation is of the form required by the extensions of the Debye–Hückel theory for concentrated solutions, and corresponds to the approximate empirical equations which hold for the activity coefficients of hydrochloric acid and calcium chloride at concentrations greater than 3N, *viz.*,

$$\left.\begin{aligned} \log f_{HCl} &= -0{\cdot}42 + 0{\cdot}18[Cl^-] \\ \log f_{CaCl_2} &= -0{\cdot}55 + 0{\cdot}20[Cl^-] \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

For the chloro-complexes of the cupric ion, Bjerrum (*loc. cit.*) was able to determine the constant B in equation (8) since at a wave-length of 436 mμ, only the tetrachloro-complex absorbs; hence the concentration of this complex could be determined from Beer's law and B could then be calculated by using an extension of Bodländer's equation. The values of the association constants could, however, still not be calculated with certainty since only an approximate estimate of the value of the constant A could be made. With the ferric chloride system, this procedure cannot be followed since there is no wave-length at which only one of the ionic species absorbs. We shall therefore make our calculations of the association complexes and of the extinction coefficients of the individual ions on the basis that in equation (7), $C = 1$, a procedure which involves no new assumptions other than those already made by Bjerrum (*loc. cit.*). Then by introducing the "Guggenheim assumption" that $f_{\mathrm{Cl^-}} = f_{\mathrm{HCl}}$ we can rewrite equation (5) in the form

$$K_n' = \frac{[\mathrm{FeCl}_n^{3-n}]}{[\mathrm{FeCl}_{n-1}^{4-n}][\mathrm{Cl}^-]} \cdot \frac{1}{f_{\mathrm{HCl}}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

in which we replace K_n by K_n' for the association constant, since non-thermodynamic assumptions have been introduced.

That this procedure may give values of the association constant (K_n') not significantly different from that of the true constant (K_n) is shown by the results of Bjerrum (*loc. cit.*) and of Näsänen (*loc. cit.*) for the chloro-complexes of the cupric ion. For this system it was found that for solutions containing hydrochloric acid $B = 0{\cdot}20$ (Bjerrum) and 0·21 (Näsänen), and for solutions containing calcium chloride $B = 0{\cdot}21$ (Bjerrum). The close agreement between these values and the values of B in equation (9), taken with the fact that Bjerrum concludes that the value of A in concentrated solutions of various chlorides must be between 0 and $-0{\cdot}5$, shows that the use of the equation corresponding to (10) for the chloro-complexes of the cupric ion would be justifiable for that system. The similarity between the cupric chloride and the ferric chloride systems suggests that a similar procedure may lead to values close to the true values of the association constants for the chloro-complexes of the ferric ion.

The experimental difficulties attendant on the determination of the association constants increase considerably as the number of complexes increases. This is particularly true if the formation constants of the higher complexes are small, as it is then necessary to make measurements in high and varying concentrations of the co-ordinating ion. The method of corresponding solutions has frequently been used for obtaining association constants from spectral data (Bjerrum, *Kgl. Danske Videnskab. Selskab., Mat.-fys. Medd.*, 1944, **21**, No. 4), and a modification of this method was used by Olerup (Thesis, Lund, 1944; *Svensk Kem. Tidskr.*, 1943, **55**, 324) for the determination of K_1 and K_2 for the chloro-complexes of iron. The method is limited in its application, however, to relatively dilute solutions of the co-ordinating ion, since it is dependent on the accurate determination of the difference between the total ligand concentration ([A]) and the concentration bound to the central ion (C_{A}). In concentrated solutions of ligand (greater than 3N) and very dilute solutions of the central ion (*ca.* 0·001N) such as must be employed for the formation of the higher chloro-complexes of iron, C_{A} is negligibly small compared with [A] and the method cannot be used.

An alternative method, which has been used in the present work, is to study the variation of the extinction coefficient with ligand concentration. This method has frequently been used for the determination of the first association constants, but the analysis of the data becomes difficult when several complexes are present. However, by introducing certain simplifying assumptions which appear to be justified in the present case, the constants can be evaluated.

Since we have shown that $\mathrm{FeCl_4^-}$ is the highest complex formed, and as there is little variation of the extinction coefficient ($\varepsilon_{\mathrm{Fe}}$) with chloride concentration in the concentration range 8—11·35M (Fig. 2), it appears probable that only the species $\mathrm{FeCl_3}$ and $\mathrm{FeCl_4^-}$ are present in these solutions. On the basis of this assumption, equations similar to those derived by Olson and Simonson (*J. Chem. Phys.*, 1949, **17**, 1322) can now be obtained.

We have assumed that $\Sigma\text{Fe} = [\text{FeCl}_4^-] + [\text{FeCl}_3]$, and it follows that for 1-cm. cells the optical density is given by

$$D = [\text{FeCl}_4^-]\varepsilon_{\text{FeCl}_4^-} + [\text{FeCl}_3]\varepsilon_{\text{FeCl}_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

and putting (4), in view of (10), in the form

$$k_4' = 1/K_4' = [\text{FeCl}_3][\text{Cl}^-]f_{\text{HCl}}/[\text{FeCl}_4^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

we obtain

$$\varepsilon_{\text{M}}(k_4' + [\text{Cl}^-]f_{\text{HCl}}) = [\text{Cl}^-]f_{\text{HCl}}\varepsilon_{\text{FeCl}_4^-} + k_4'\varepsilon_{\text{FeCl}_3} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

in which $\varepsilon_{\text{M}} = D/\Sigma\text{Fe}$.

Equation (13) contains three unknowns k_4', $\varepsilon_{\text{FeCl}_4^-}$, and $\varepsilon_{\text{FeCl}_3}$. From measurements at three different chloride concentrations in the range 8—11·35N, and solving the three simultaneous equations, we obtain.

$$k_4' = \frac{\varepsilon'_{\text{M}}A_1(A_2 - A_3) + \varepsilon_{\text{M}}''A_2(A_3 - A_1) + \varepsilon_{\text{M}}'''A_3(A_1 - A_2)}{\varepsilon_{\text{M}}'(A_2 - A_3) + \varepsilon_{\text{M}}''(A_3 - A_1) + \varepsilon_{\text{M}}'''(A_1 - A_2)} \quad . \quad . \quad . \qquad (14)$$

where ε_{M}', ε_{M}'', $\varepsilon_{\text{M}}'''$ and A_1, A_2, A_3 are the observed average extinction coefficients and chloride activities, respectively, for the three solutions.

From the value of k_4' thus determined, $\varepsilon_{\text{FeCl}_4^-}$ and $\varepsilon_{\text{FeCl}_3}$ could be found in a similar way from measurements on two solutions of different chloride-ion activity. We have, however, preferred an alternative method. The plot of ε_{M} against $[\text{Cl}^-]f_{\text{HCl}}$ will give, as is evident from equation (13), a rectangular hyperbola (see Fig. 2) with asymptotes $x = -k_4'$ and $y = \varepsilon_{\text{FeCl}_4^-}$, the intercept on the ordinate being $\varepsilon_{\text{FeCl}_3}$. Knowing k_4', however, we may plot the function $\varepsilon_{\text{M}}(k_4' + [\text{Cl}^-]f_{\text{HCl}})$ against $[\text{Cl}^-]f_{\text{HCl}}$, which should give a straight line of slope $\varepsilon_{\text{FeCl}_4^-}$ and an intercept of $k_4'\varepsilon_{\text{FeCl}_3}$. The value of $\varepsilon_{\text{FeCl}_4^-}$ may be obtained from the slopes of the lines with good accuracy, but the value of the intercept, which gives $\varepsilon_{\text{FeCl}_3}$, is very dependent on the " best " straight line chosen. The value of the intercept was therefore calculated by the method of least squares. This method may be extended to less concentrated solutions of hydrochloric acid where a third complex FeCl_2^+ will also be present. We then have, ultimately,

$$\varepsilon_{\text{M}}\{k_3'k_4' + k_4'[\text{Cl}^-]f_{\text{HCl}} + ([\text{Cl}^-]f_{\text{HCl}})^2\} = ([\text{Cl}^-]f_{\text{HCl}})^2\varepsilon_{\text{FeCl}_4^-} + k_4'[\text{Cl}^-]f_{\text{HCl}}\varepsilon_{\text{FeCl}_3} + \varepsilon_{\text{FeCl}_2^+} \quad . \qquad (15)$$

in which k_3' is defined in a similar manner to k_4', *viz.*,

$$k_3' = [\text{FeCl}_2^+][\text{Cl}^-]f_{\text{HCl}}/[\text{FeCl}_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

and in which k_3' and $\varepsilon_{\text{FeCl}_2^+}$ are the only unknowns. Values of these may therefore be obtained from measurements at two different chloride activities.

Results and Discussion.—The spectra of solutions of ferric chloride at various concentrations of hydrochloric acid and at a concentration of ferric chloride of approximately 0·002M are shown in Fig. 3. The spectra resemble those published by Metzler and Myers (*loc. cit.*). The plot of the function $\varepsilon_{\text{M}}(k_4' + [\text{Cl}^-]f_{\text{HCl}})$ against $[\text{Cl}^-]f_{\text{HCl}}$ [equation (13)] is given in Fig. 4 for four typical wave-lengths, and the very good straight lines obtained show that the assumption that only two complexes are present in solutions of hydrochloric acid of concentration greater than 8·0M is justified. The five points on each straight line refer to measurements on solutions of concentration 8·20, 8·65, 9·86, 10·60, and 11·35M in hydrochloric acid, and values of K_4' have been calculated from results obtained at 10 mμ intervals between 260 and 400 mμ. Values of K_3' were similarly calculated at different wave-lengths from measurements on solutions containing hydrochloric acid of concentration 5·08 and 3·33M by means of equation (15). The mean values of K_3' and K_4' are given in the Table along with the values of K_1, K_2, and K_3 given by Rabinowitch and Stockmayer (*loc. cit.*), and by Olerup *locc. cit.*).

Formation constants of the iron(III) *chloro-complexes.*

K_1	K_2	K_3	K_4'	Conditions *	Author
4·2	1·3	0·04	—	$I = 1$, $T = 26·7°$	Rabinowitch and Stockmayer
30	4·5	0·1	—	$I = 0$, $T = 25°$	
5·7	2·0	0·87	—	2M-HClO_4, $I = 2$, $T = 20°$	Olerup
		K_3'			
—	—	0·73	0·0105	$I = 0$, $T = 20°$	This paper

* I = Ionic strength.

A feature of these results is the apparently low value of K_4', and the reason for this result may be sought by calculating the values of the "ligand effect" by Bjerrum's method (Thesis, Copenhagen, 1941). In this treatment, the ratio of the consecutive formation constants is regarded as the product of the statistical (S) and ligand (L) effects, *viz.*,

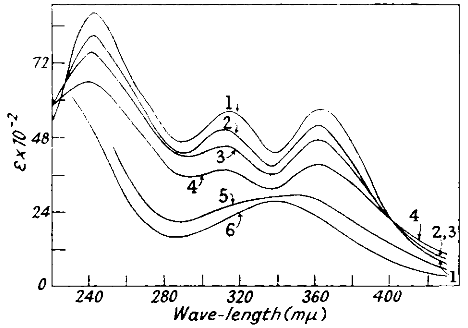
$$\log (K_n/K_{n+1}) = S_{n.n+1} + L_{n.n+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where $S = \log [(N - n + 1)(n + 1)/(N - n)n]$. Calculation of L for a co-ordination number (N) of 6, the values 30, 4·5, 0·73, and 0·0105 being used for K_1, K_2, K_3, and K_4, respectively, gives $L_{1,2} = 0{\cdot}44$, $L_{2,3} = 0{\cdot}52$, and $L_{3,4} = 1{\cdot}59$, or for a co-ordination number of four $L_{3,4} = 1{\cdot}41$. For a given series of complexes the ligand effect should be a constant, and Bjerrum (Thesis, Copenhagen, 1941; *Kgl. Danske Videnskab. Selskab., Mat.-fys. Medd.*, 1946, **22**, No. 18) has shown this to be so for several systems. Furthermore, when the co-ordinating group is an ion, the ligand effect should be a function of the electrostatic work done in changing the complex from, for example, FeCl_n^{3-n} to $\mathrm{FeCl}_{n+1}^{2-n}$, and from the theory of the electrostatic field effect (see N. Bjerrum, *Z. physikal. Chem.*, 1923, **106**, 219; Kirkwood and Westheimer, *J. Chem. Phys.*, 1938, **6**, 506, 513), we may write for a singly charged co-ordinating ion

$$L_{n,n+1} = e^2/DakT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

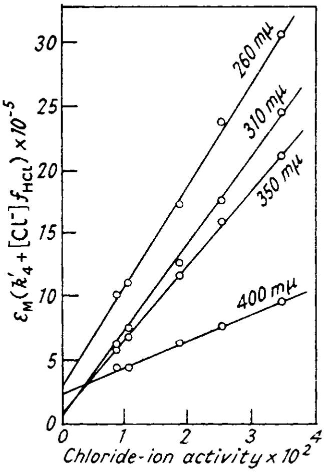
where e is the electronic charge, k the Boltzmann constant, T the temperature, D the effective dielectric constant, and a the distance between the charged groups. In arriving at equation (18) we have assumed that the "Rest effect" (Bjerrum, Thesis, Copenhagen, 1941) is negligibly small and that the iron(III) chloro-complexes are ionic, as suggested by the magnetic moment of $\mathrm{FeCl_4}^-$ determined by Nyholm (*J.*, 1950, 851) and by Metzler and Myers (*loc. cit.*). Calculation of a from $L_{1,2}$ and $L_{2,3}$, D for water being taken as 78, gives the values 7 and 6 Å. The good agreement between these values reflects the agreement between $L_{1,2}$ and $L_{2,3}$ and the values, although somewhat high, are of the order of magnitude to be expected for the distance between the chloride ions in $\mathrm{FeCl_3}$. A similar calculation for $L_{3,4}$ leads to a very low and improbable value for a (2 Å). It would therefore appear that the values of $L_{1,2}$ and $L_{2,3}$, and hence of K_1, K_2, and K_3, may be regarded as normal values, the variation of the association constants being of the order expected. On the other hand, $L_{3,4}$ is higher and K_4 lower (relative to K_3) than would be predicted. Such behaviour may be attributed to a change in the co-ordination number of the central ion from six to four at $\mathrm{FeCl_3}$, *i.e.*, a change on the addition of $\mathrm{Cl^-}$ from $\mathrm{FeCl_3(H_2O)_3}$ to

FIG. 3. *Variation of extinction coefficient with wave-length for various concentrations of hydrochloric acid at constant concentration of ferric chloride* (0·002M).



1, 11·35M; 2, 10·60M; 3, 9·86M; 4, 8·65M; 5, 5·08M; 6, 3·33M.

FIG. 4. *Variation of the function* $\varepsilon_M(k'_4 + [\mathrm{Cl}^-]f_{\mathrm{HCl}})$ *with chloride-ion activity for four typical wave-lengths.*



$FeCl_4^-$ as is suggested by Friedman's results (*loc. cit.*) discussed above. If this conclusion is correct, the values of $L_{3,4}$, obtained above, can have no theoretical significance, since in the ratio K_3/K_4 the two association constants refer to different structures.

The values of $\varepsilon_{FeCl_4^-}$, ε_{FeCl_3}, and $\varepsilon_{FeCl_2^+}$ obtained by equations (13) and (15), together with the values of $\varepsilon_{FeCl^{2+}}$ and $\varepsilon_{Fe^{3+}}$ taken from Olerup's results (Thesis, Lund, 1944) are given in Fig. 5. In the range 400—440 mμ Rabinowitch and Stockmayer's values (*loc. cit.*) for ε_{FeCl_3} and $\varepsilon_{FeCl_2^+}$ are also shown, and the agreement of the two sets of results over this range is very satisfactory, particularly in view of the different assumptions made in the two methods of calculation. This confirmation of Rabinowitch and Stockmayer's value of ε_{FeCl_3} at 400 mμ invalidates Olerup's criticism (*loc. cit.*, p. 76) that this value was too high. The similarity of the spectra of $FeCl^{2+}$ and $FeCl_2^+$, which both have a maximum absorption at 340 mμ, although $\varepsilon_{FeCl_2^+} > \varepsilon_{FeCl^{2+}}$, and the broad absorption band of $FeCl_3$ in the range 380—440 mμ, confirms Metzler and Myers's qualitative predictions (*loc. cit.*). The calculated spectra of $FeCl_4^-$ and $FeCl_3$ given in Fig. 4 are in general agreement with those of Brealey and Uri (*loc. cit.*) for alcoholic solutions containing perchloric acid apart from the small maximum in ε_{FeCl_3} which we obtain at 340 mμ. The values of the extinction coefficients given by Brealey and Uri are, however, somewhat higher than those obtained for aqueous solutions.

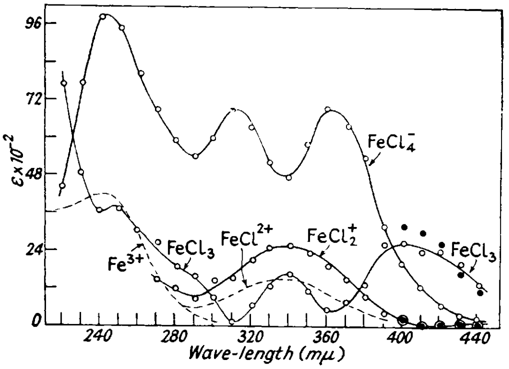


FIG. 5. *Molecular extinction coefficients at various wave-lengths for the species* $FeCl_4^-$, $FeCl_3$, $FeCl_2^+$, $FeCl^{2+}$, *and* Fe^{3+}. ○ *Values calculated from results in Fig.* 3 *by authors.* ● *Rabinowitch and Stockmayer's results. Broken line : Olerup's data.*

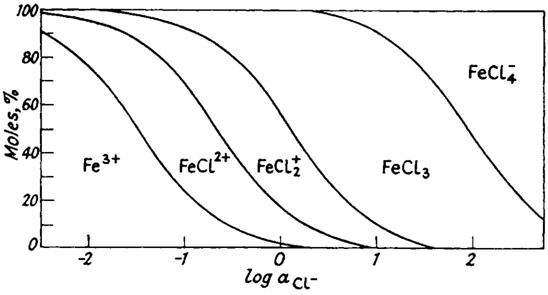


FIG. 6. *Distribution of the ferric ion among the chloro-complexes at various chloride-ion activities.*

From the values of the four constants, the distribution of the ferric ion among the four complexes may be calculated, and this is shown diagrammatically in Fig. 6.

The extension of this method to more dilute solutions of hydrochloric acid in order to obtain values of K_1', K_2', and $\varepsilon_{FeCl^{2+}}$ is rendered difficult by the formation of the hydroxy-complexes. If these are eliminated by the addition of perchloric acid to give a concentration of 3M, the dissociation constants at $I = 0$ cannot be determined since the activities of hydrochloric acid in perchloric acid solutions are not known. We have attempted to obtain values at constant ionic strength by the addition of sodium perchlorate, but this produces a marked shift in the absorption curve to higher ε values, an effect which has also been observed by Olson and Simonson (*loc. cit.*).

EXPERIMENTAL

Spectroscopic Measurements.—Spectra were measured at 20° ± 1° by means of a Unicam S.P. 500 spectrophotometer and matched 2, 10, 20, and 40 mm. cells.

Preparation of Materials.—Aqueous solutions of ferric perchlorate were prepared by Lindstrand's method (*Z. anorg. Chem.*, 1936, **230**, 187). Crystals of hydrated ferric perchlorate were prepared by adding 5 g. of reduced iron to 45 ml. of 60% perchloric acid (3 ml. excess) in an evaporating basin (addition of acid to iron gives a brown sludge which is difficult to dissolve). To ensure that the iron was fully oxidised, 2 ml. of hydrogen peroxide (20-vol.) were added, and the solution heated to 70°. The solution was filtered (No. 3 sintered-glass filter), evaporated until crystallization occurred and fumes of perchloric acid were evolved, and placed in a vacuum-desiccator (P_2O_5; NaOH). The crystals as first prepared were light brown, but on standing *in vacuo* over P_2O_5 for four weeks they changed through yellow to white with a mauvish tinge. The yellow crystals had the composition $Fe(ClO_4)_3,10H_2O$.

Solutions of anhydrous ferric perchlorate in dry ethyl alcohol were prepared by reaction of a solution of anhydrous silver perchlorate (Hill, *J. Amer. Chem. Soc.*, 1921, **43**, 254) in a closed system with the stoicheiometric quantity of a solution of anhydrous ferric chloride in dry alcohol. They were deep red and all attempts to promote crystallisation failed.

The ferric chloride was of A. R. quality and was generally purified by sublimation although this did not appear to be essential. The perchloric acid and hydrochloric acid were of A.R. quality and the lithium chloride of reagent quality. Absolute ethyl alcohol suitable for spectroscopic measurements was prepared either by the calcium method or by the aluminium amalgam method.

The concentration of the solutions containing ferric chloride and hydrochloric acid was determined by gravimetric estimation of the iron and chloride. The values of the activity coefficients for hydrochloric acid in concentrated aqueous solutions were taken from Akerlöf and Teare's data (*J. Amer. Chem. Soc.*, 1937, **59**, 1855).

We wish to thank Dr. J. Chatt for helpful criticism and Mrs. J. Lewis for assistance with the numerical computation.

THE UNIVERSITY, NOTTINGHAM. [*Received, October* 31*st*, 1952.]