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Association of Ferric Ions with Chloride, Bromide and Hydroxyl Ions (A Spectroscopic Study)

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I. Introduction

Recent studies have shown that solutions of the salts of polyvalent metals often contain not only free ions and undissociated molecules, but also diverse intermediate ionic species. For a number of cations equilibrium constants have been determined, usually by electrochemical methods, for several successive steps of association with different anions; we may refer, *e. g.*, to the work on Cd^{2+} by Leden¹ and on Pb^{2+} by Fromherz.² In the case of the most important trivalent ion, Fe^{3+} , Lamb and Jacques³ have determined the constants of stepwise association with OH^- ions to FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_3$. Their results show that unless the medium is extremely acid, all ferric salt solutions contain measurable quantities of the two intermediate hydrolysis products FeOH^{2+} and $\text{Fe}(\text{OH})_2^+$. (The final product, $\text{Fe}(\text{OH})_3$, on the other hand, is practically insoluble, and as soon as its concentration exceeds about 2×10^{-9} mole/l., the original molecular solution transforms itself more or less rapidly into a colloidal solution or suspension.) As to the association of ferric ions with anions other than OH^- , our knowledge is as yet very incomplete. Estimates of the first association constant of Fe^{3+} ions with Cl^- ions have been made by Bray and Hershey⁴ and Möller⁵ from potentiometric measurements; Bent and French⁶ and Edmonds and Birnbaum⁷ have calculated the first association constant of Fe^{3+} ions with CNS^- ions from spectrophotometric observations. Bent and French⁶ have used FeCNS^{2+} also as a colored indicator for an indirect determination of the association constant of Fe^{3+} ions with Cl^- ions.

On the other hand, it is known that sometimes the association of Fe^{3+} ions goes much further, producing anions of the type of $\text{Fe}(\text{CNS})_4^-$ (*cf.* Moeller⁸ and Schlesinger⁸), or of the more familiar

$\text{Fe}(\text{CN})_6^{3-}$. Without doubt, the formation of these negative ions is preceded by that of the intermediary positive ions and neutral molecules; but no quantitative data are available on this stepwise association.

We have attempted to obtain some information on the association of Fe^{3+} ions, mainly with Cl^- ions, by spectrophotometric measurements. It was mentioned above that this method was already used by Bent and French⁶ and Edmonds and Birnbaum⁷ in the study of the intensely colored thiocyanate complexes. Lamb and Jacques,³ too, have used colorimetry (among other methods) in their investigation of the hydrolysis of ferric ions, on the assumption that when colloidal ferric hydroxide is present in ferric salt solutions, it alone is responsible for their color.

However, most ferric salt solutions are yellow even at *pH* values which preclude the formation of colloidal hydroxide, and in the absence of anions (such as CNS^-), with which they form intensely colored complexes. The yellow color has been attributed, without sufficient proof, sometimes to neutral molecules (*e. g.*, FeCl_3 or Fe_2Cl_6) and sometimes to complex anions (*e. g.*, FeCl_6^{3-}). However, a solution of ferric chloride, for example, can contain all the species Fe^{3+} , FeCl^{2+} , FeCl_2^+ , FeCl_3 , FeCl_4^- , FeCl_5^{2-} and FeCl_6^{3-} , in addition to the inevitable ions FeOH^{2+} and $\text{Fe}(\text{OH})_2^+$; and there is no reason to make a single one of these species, *e. g.*, FeCl_3 or FeCl_6^{3-} , responsible for the color unless such a correlation is confirmed by quantitative spectroscopic evidence. In the case of the ferric thiocyanate, Bent and French⁶ showed that the first association product, FeCNS^{2+} , is intensely colored, and accounts for the greater part of the light absorption at low concentrations of the thiocyanate.

In the course of the present study, we found indications that most, if not all, complex forms of the ferric ion have absorption bands either in the near ultraviolet, or in the blue-violet part of the visible spectrum. Since the wings of the ultraviolet bands also extend into the visible, the color of a given ferric salt solution can be due to any

- (1) I. Leden, *Z. physik. Chem.*, **188A**, 160 (1941).
- (2) H. Fromherz, *ibid.*, **153A**, 382 (1931).
- (3) A. B. Lamb and A. G. Jacques, *THIS JOURNAL*, **60**, 977, 1215 (1938).
- (4) W. C. Bray and A. V. Hershey, *ibid.*, **56**, 1889 (1934).
- (5) M. Möller, *J. Phys. Chem.*, **41**, 1123 (1937).
- (6) H. E. Bent and C. L. French, *THIS JOURNAL*, **63**, 568 (1941).
- (7) S. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).
- (8) H. I. Schlesinger, *ibid.*, **63**, 1765 (1941).

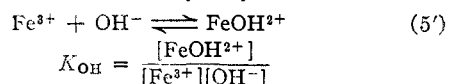
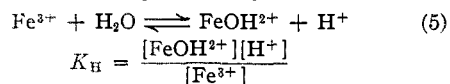
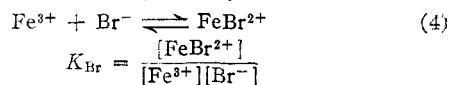
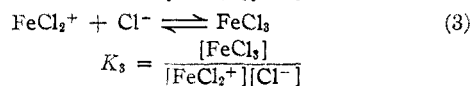
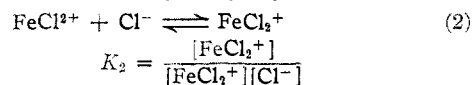
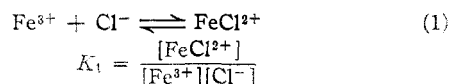
or all of a multitude of associated products, and only a detailed investigation of the spectrum at different concentrations, acidities, and temperatures can give some indication as to the true origin of the absorption bands.

Von Kiss, Abraham and Hegedüs⁹ have recently published a spectrophotometric investigation of the solutions of ferric chloride, sulfate, thiocyanate, and other ferric salts, but the fact that they did not pay sufficient attention to all factors affecting the association equilibria detracts from the quantitative value of their extinction curves. Some of these curves were determined under conditions which admittedly made the slow formation of colloidal hydroxide inevitable: in others, the effect of intermediate ions, such as FeOH^{2+} , should have been considered. The suggestion of v. Kiss and co-workers⁹ that the absorption bands of ferric salt solutions are due, at the high concentrations of the anions, to the complex anions FeCl_6^{3-} , $\text{Fe}(\text{CN})_6^{3-}$, etc., and at the lower concentrations, to the neutral molecules, FeCl_3 , $\text{Fe}(\text{CN})_3$, etc., cannot be accepted in absence of any attempt on their part to give a quantitative interpretation of the absorption curves.

In the study of the oxidation-reduction potentials of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system, the depressing effect of chloride ions on E^0 has been attributed to the formation of the associated ionic species FeCl_2^{2+} (*cf.* Bray and Hershey,⁴ Möller⁵). Again, the assumption of only one association step is unwarranted. However, such a simplification is less dangerous here than in the study of the absorption spectra. In the latter case, a relatively small proportion of a highly colored product can play havoc with the absorption curves. In electrochemical measurements, on the other hand, the effect of each associated ionic species is strictly proportional to its concentration, so that small quantities of the higher associates cannot exercise a strong influence on the potential.

In the present paper, we have determined the absorption spectra of ferric salt solutions under controlled conditions of acidity, ionic strength and temperature, by means of the Hardy¹⁰ automatic recording spectrophotometer,¹¹ and have attempted to calculate from these results the ther-

modynamic constants of the following association equilibria:



Equations (5) and (5') are two formulations of the same first step of hydrolysis.

All measurements with the Hardy spectrophotometer were made at $26.7 \pm 1^\circ$. The ferric solutions were analyzed by the Zimmermann-Reinhardt method, with the permanganate solution standardized against sodium oxalate. The acids—perchloric, hydrochloric and hydrobromic—were titrated with sodium hydroxide standardized against acid potassium phthalate. The saturated sodium perchlorate solution was prepared by the action of perchloric acid on pure solid sodium hydroxide; its concentration was determined from the solubility data of Cornec and Dickeley.¹²

II. The Spectrum of the Ferric Ion $\text{Fe}_{\text{aq}}^{3+}$

Perchlorates and nitrates normally show the least tendency for complex formation. The faint purple color of solid ferric nitrate and perchlorate as well as of strongly acid solutions of these salts is indicative of the absorption spectrum of the free (hydrated) Fe^{3+} ion.

We found no spectroscopic indications of complexes of Fe^{3+} ions with perchlorate ions in aqueous solutions up to $[\text{ClO}_4^-] = 3$ mole/l. (The yellow color of ferric perchlorate solutions in organic solvents, *e. g.*, methyl alcohol, makes it probable that such complexes are present there, although this color may also be due to alcoholysis.) However, even in comparatively strong perchloric acid, aqueous ferric perchlorate solutions

(9) Von Kiss, Abraham and Hegedüs, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

(10) A. C. Hardy, *J. Opt. Soc. Am.*, **25**, 305 (1935).

(11) We thank the Staff of the Color Measurements Laboratory, M. I. T., for their friendly cooperation.

(12) E. Cornec and Dickeley, *Bull. soc. chim.*, **41**, 1017 (1927); *Compt. rend.*, **184**, 1555 (1927).

are bound to contain appreciable quantities of association products of Fe^{3+} ions and hydroxyl ions, whose contribution to the absorption spectrum must be deduced to obtain the true extinction curve of the Fe^{3+} ions. With this purpose in mind, we have measured the absorption spectra of solutions of ferric perchlorate (prepared by dissolution of reprecipitated ferric hydroxide in perchloric acid) under varying conditions of acidity, ($p\text{H}$), ionic strength, (μ), and temperature. Sodium perchlorate was used for the adjustment of μ , and perchloric acid for that of $p\text{H}$.

Figure 1 shows the effect of a (comparatively small) change in $p\text{H}$, at constant μ , on the visible absorption spectrum of ferric perchlorate; the ordinates are the "average" absorption coefficients $\bar{\epsilon}$, defined by the equation

$$\bar{\epsilon} = \frac{1}{d[\text{Fe}^{3+}]_0} \log_{10} \frac{I_0}{I} \quad (6)$$

where d is the thickness of the cell and $[\text{Fe}^{3+}]_0$ the total concentration of trivalent iron. Figure 1 shows that the intensities of two bands, one with a maximum above $700 \text{ m}\mu$ and one at $540 \text{ m}\mu$, are independent of $p\text{H}$; these bands can thus be considered as belonging exclusively to Fe^{3+} ions. The peak at $407 \text{ m}\mu$ also is due to this ion, since it becomes sharper with increasing acidity; but it is superimposed upon an absorption of a different origin, which begins at $530 \text{ m}\mu$ and rises steadily toward the ultraviolet. This absorption increases with decreasing acidity, and must be attributed to the ion FeOH^{2+} . The divergence of the $\bar{\epsilon}$ -curves corresponding to different $p\text{H}$'s is even stronger in the ultraviolet, as shown in the inset in Fig. 1. (The curves III and IV are drawn on a semi-logarithmic scale in order to allow the representation of the strong absorption in the ultraviolet in the same diagram with the weak absorption in the visible.) The full lines in the ultraviolet were obtained by means of a photographic spectrophotometer with variable aperture (Hilger Spekker); the dotted lines represent an interpolation between these data and the results obtained by means of Hardy's recording spectrophotometer. Curves III and IV indicate that the relative contribution of FeOH^{2+} to $\bar{\epsilon}$ reaches its maximum somewhere around $375 \text{ m}\mu$; further in the ultraviolet the increasingly strong absorption by Fe^{3+} ions becomes dominant. V. Kiss and co-workers⁹ thought that the absorption curve of ferric perchlorate in 2.55 molar perchloric acid could safely be attributed to the free (hy-

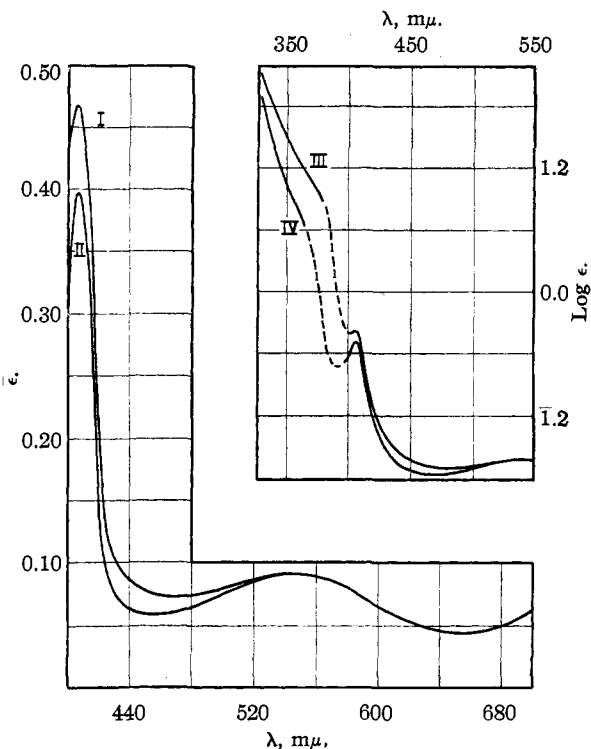


Fig. 1.—Average absorption coefficient of $(\text{Fe}^{3+} + \text{FeOH}^{2+})$.

	Concentrations in mole/liter			
	$\text{Fe}(\text{ClO}_4)_3$	HClO_4	NaClO_4	
Curve I	0.100	0.492	1.092	2.184
Curve II	.200	.984	...	2.184
Curve III	.050	.25	0.25	0.80
Curve IV	.050	.5080

drated) ions Fe^{3+} , and they therefore used it as a "reference curve" in the discussion of the absorption spectra of all other ferric salts. It follows from the above discussion that this curve still contains, in the region $300\text{--}500 \text{ m}\mu$, a contribution due to the FeOH^{2+} ions. In extinction curves obtained by v. Kiss in more dilute acids, *e. g.*, 0.6 m perchloric or 0.2 m hydrochloric, the contributions of the ions FeOH^{2+} and $\text{Fe}(\text{OH})_2^+$ are much heavier; maxima shown by many of these curves at about $330\text{--}340 \text{ m}\mu$ may be due to these intermediate products of hydrolysis rather than to the complexes involving the specific anion of the salt.

For a quantitative separation of the absorption of Fe^{3+} from that of FeOH^{2+} , we write

$$\bar{\epsilon}[\text{Fe}^{3+}]_0 = \epsilon_{\text{Fe}^{3+}}[\text{Fe}^{3+}] + \epsilon_{\text{FeOH}^{2+}}[\text{FeOH}^{2+}] \quad (7)$$

Using eq. (5) and considering that, under the conditions of our experiments, $[\text{Fe}^{3+}] \gg [\text{FeOH}^{2+}]$ and $[\text{H}^+] \gg [\text{FeOH}^{2+}]$, we can transform (7) into

$$\bar{\epsilon}[\text{Fe}^{3+}]_0 = \epsilon_{\text{Fe}^{3+}}[\text{Fe}^{3+}]_0 + \epsilon_{\text{FeOH}^{2+}} \frac{K_{\text{H}}[\text{Fe}^{3+}]_0}{[\text{H}^+]_0} \quad (7a)$$

or

$$\epsilon = \epsilon_{\text{Fe}^{3+}} + \epsilon_{\text{FeOH}^{2+}} \frac{K_{\text{H}}}{[\text{H}^+]_0} \quad (7b)$$

where $[\text{Fe}^{3+}]_0$ is the total concentration of iron and $[\text{H}^+]_0$ the hydrogen ion concentration due to perchloric acid (*i. e.*, with the neglect of the hydrogen ions produced by hydrolysis).

According to (7a) or (7b), $\epsilon_{\text{Fe}^{3+}}$ can be determined by comparison of the absorption curves of two solutions for which K_{H} has the same value. This means, first of all, solutions of equal ionic strength, since K_{H} , like all equilibrium constants involving ions, depends on the ionic strength. It will be shown in Section III that K_{H} also depends to a certain extent on the specific composition of the solution. Neglecting this effect, we calculate $\epsilon_{\text{Fe}^{3+}}$ from the curves in Fig. 1, which correspond to two pairs of solutions of different composition, but with equal ionic strength. Table II contains the absorption coefficients. Figure 2 shows, on a semi-logarithmic scale, the absorption curve of Fe^{3+} ions. The characteristic narrow band at 407 $m\mu$ can be obliterated by the $\text{Fe}(\text{OH})^{2+}$ absorption in solutions of insufficient acidity; it was missed by Hardtmann¹³ and v. Kiss, Abraham and Hegedüs,⁹ although the latter worked with $p\text{H} < 0$. The segment of the curve below 275 $m\mu$ has been taken from the data of v. Kiss and co-workers.⁹ In this region, the absorption coefficients are of the order of 10^3 to 10^4 , and must therefore belong to the ion Fe^{3+} , rather than to complexes of the type of FeOH^{2+} . (At the comparatively high acidities used by v. Kiss, 2.55 *m* perchloric acid/l., the concentration of FeOH^{2+} is of the order of 0.1% of that of Fe^{3+} , and no compounds are known with molar extinction coefficients of the order of 10^6 or 10^7 .) The dotted segments of the curve are interpolations.

The absorption spectrum of the Fe^{3+} ion (more exactly, of the ion $\text{Fe}_{\text{aq}}^{3+}$) thus consists of a heavy double-peaked absorption band at 200–240 $m\mu$, and of three much weaker absorption bands in the visible, of which one, at 407 $m\mu$, is remarkable by its sharpness (half-width about 20 $m\mu$), whereas the other two are much more diffuse (the band at 550 $m\mu$, which is responsible for the faint purple color of the ferric ions, has a half-width of about 135 $m\mu$).

The electronic state of the free Fe^{3+} ion is $d^5, ^6\text{S}$, and the same ground state can be attributed to the

hydrated ion. It seems plausible to ascribe the heavy absorption bands in the far ultraviolet to the permitted transitions $d^5 \rightarrow d^4p$, and the weak absorption bands in the visible to the forbidden transitions $d^5 \rightarrow d^4s$ and $d^5 \rightarrow d^5$. (The sharpness of the 407 $m\mu$ band, reminiscent of the absorption bands of rare earths, may be understood by attributing it to a $d^5 \rightarrow d^3$ transition, which does not change the size of the ion and therefore does not interfere appreciably with the structure of the hydration sphere.)

III. The FeOH^{2+} Ion; Spectrum and Thermodynamic Constants

According to eq. (7), our measurements of $\bar{\epsilon}$ in mixtures of Fe^{3+} and FeOH^{2+} can give only the product $\epsilon_{\text{FeOH}^{2+}} K_{\text{H}}$, and not the two constants separately. This is due to the fact that in the present study we are confined to the region where $[\text{FeOH}^{2+}] \ll [\text{Fe}^{3+}]$, and are prevented by the danger of the formation of colloidal hydroxide, from extending the measurements toward higher $p\text{H}$ -values, where "saturation" of FeOH^{2+} should begin to manifest itself. Table II contains the values of $K_{\text{H}}\epsilon_{\text{FeOH}^{2+}}$ for $\mu = 2.184$ and Fig. 2 shows a semi-logarithmic plot of them. The true extinction curve of FeOH^{2+} could be obtained from this plot by shifting the scale of ordinates by $\log K_{\text{H}}$. Values of K_{H}^0 for the ionic strength zero have been given by Lamb and Jacques³ and Bray and Hershey⁴: $K_{\text{H}}^0 = 3.5 \times 10^{-3}$ (L. J.) or 6×10^{-3} (B. H.). In Fig. 8 we have plotted the association constant of Fe^{3+} ions with Cl^- ions, K_1 , against $\sqrt{\mu}$. Assuming that the dependence of K_{H} on $\sqrt{\mu}$ is about the same as that of K_1 , we obtain, from the above values of K_{H}^0 , values of the order of 0.7 to 1.2×10^{-3} (for $\mu = 2$). The scale on the left side of Fig. 2 gives the absorption coefficients of FeOH^{2+} calculated on the assumption that K_{H} (at $\mu = 2.184$) is 1×10^{-3} . It will be noted that $\epsilon_{\text{FeOH}^{2+}}$ reaches about 5000 at 325 $m\mu$; this high value shows that this wave length must be close to the peak of the FeOH^{2+} absorption band. The maximum of the main Fe^{3+} absorption band lies, according to Fig. 2, at about 240 $m\mu$, where $\epsilon_{\text{Fe}^{3+}}$ also reaches a value of about 5000.

According to equation (7b), the apparent extinction coefficient of solutions containing Fe^{3+} and $\text{Fe}(\text{OH})^{2+}$ should be independent of $[\text{Fe}^{3+}]_0$, as long as K_{H} is a constant. In other words, solutions of ferric perchlorate should under these

(13) E. Hardtmann, Diss., Leipzig, 1922; cf. J. Abraham, *Acta chem., min., phys. Univ. Szeged*, **6**, 272 (1928).

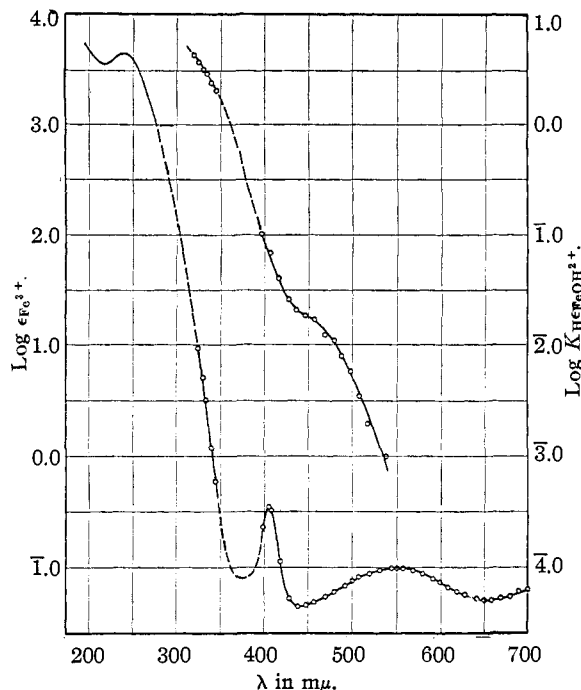


Fig. 2.—Absorption curves of Fe^{3+} (left) and FeOH^{2+} (right). The scale to the left is for the Fe^{3+} curve and applies also to the FeOH^{2+} curve if K_H is assumed to be equal to 1×10^{-3} . The scale to the right is for the product $K_H \epsilon_{\text{FeOH}^{2+}}$.

conditions obey Beer's law. We found, however, that deviations from Beer's law occur even if μ is kept constant, thus indicating that K_H is not determined uniquely by μ , but also depends on the specific composition of the solution, which is not unexpected at the high ionic strengths necessarily used in this investigation.

Figure 3 is a plot of the average absorption coefficient against $[\text{Fe}^{3+}]_0$, for several different wave lengths. It shows that whereas the absorption of 550 mμ, which is due entirely to Fe^{3+} , obeys Beer's law, ($\bar{\epsilon} = \text{const.}$), the absorptions at 400, 420, 430 and 450 mμ, which are due to an appreciable extent to FeOH^{2+} ions, show considerable deviations, indicating changes in the relative concentration of these ions. The absorption at 407 mμ, where the peak of the Fe^{3+} absorption band is situated, is relatively less affected than that on both sides of this peak, at 400 and 420 mμ. The changes in $\bar{\epsilon}$, shown by Fig. 3, occur despite the constancy of μ , when ferric perchlorate replaces sodium perchlorate. This exchange involves a considerable decrease in the total concentration of ClO_4^- ions, six moles of sodium perchlorate being replaced by one mole of ferric perchlorate. It is possible that this de-

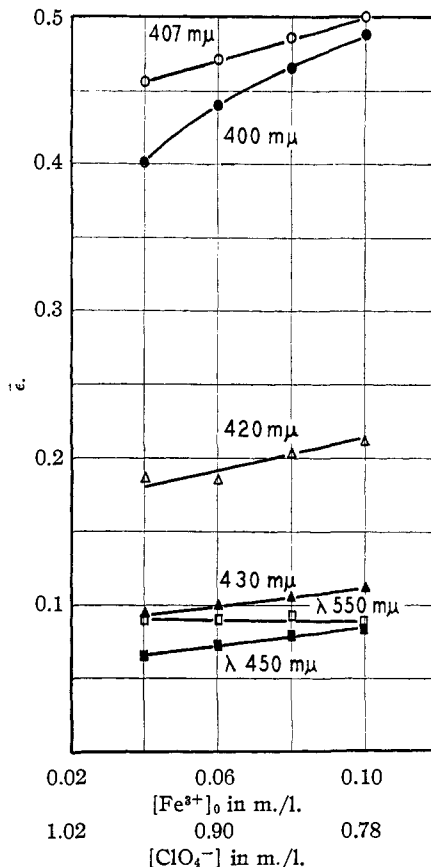


Fig. 3.—Deviation of ferric perchlorate solutions from Beer's law at constant acidity and ionic strength: $[\text{HClO}_4] = 0.48$ m./l.; $\mu = 1.06$.

crease in $[\text{ClO}_4^-]$, rather than the simultaneous increase in $[\text{Fe}^{3+}]_0$, is the primary cause of the increase in K_H (which is indicated by the upward trend of the curves in Fig. 3).

Subtracting from the $\bar{\epsilon}$ -values in Fig. 3 the $\epsilon_{\text{Fe}^{3+}}$ values from Fig. 2, and multiplying by $[\text{H}^+]$ ($= 0.48$), we obtain, according to equation (7b), the values of $K_H \epsilon_{\text{FeOH}^{2+}}$. They are shown in Fig. 4. This figure indicates that K_H changes by about 40% when we pass from a solution containing 0.04 m./l. Fe^{3+} ions and 0.96 m./l. ClO_4^- ions to one containing 0.10 m./l. Fe^{3+} and 0.78 m./l. ClO_4^- ions, despite the fact that $p\text{H}$ and μ remain constant.

A quantitative treatment of individual ion activities in these solutions is at present not possible, but the direction of the observed change in hydrolysis with increasing $[\text{ClO}_4^-]$ is that to be expected from Brönsted's principle¹⁴ that specific ion interactions between two ions of unlike sign make much larger contributions to the activity

(14) J. N. Brönsted, *This Journal*, **44**, 877 (1922).

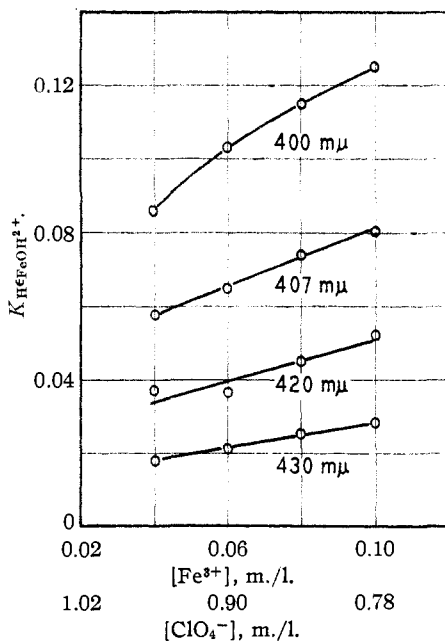


Fig. 4.—Variation in K_H with the composition of $\text{Fe}(\text{ClO}_4)_3$ solutions at constant pH and μ , derived from absorption measurements at different wave lengths.

coefficients than interactions between ions of like sign. On this principle, the important interactions affecting the hydrolysis equilibrium eq. (5), should be those between perchlorate ions and H^+ , FeOH^{2+} , and Fe^{3+} ions. Of these three interactions, the first two, which increase the activities of the products of hydrolysis, should cooperate in causing a decrease in K_H , with increasing perchlorate concentration, whereas the third should tend to increase it. Since the interactions involving H^+ ions are especially large (as is shown, for example, by a comparison of the activities of the hydrogen halides and the alkali halides), it is to be expected that the resulting effect of an increase in the concentration of perchlorate ions, at a constant ionic strength, will be to reduce the apparent hydrolysis constant K_H , which is just the direction of the observed effect. The magnitude of the observed effect is such that it might possibly be ascribed to this cause, without the necessity of postulating the existence of any additional equilibria; alternative explanations, however, can be advanced.^{14a}

It was mentioned in Section II that we neg-

(14a) One additional equilibrium which could explain the observed deviations from Beer's law would be $\text{FeOH}^{2+} + \text{Fe}^{3+} \rightleftharpoons [\text{FeOHFe}]^{5+}$. Reactions of this type have been postulated to occur in ferric, chromic and aluminum salt solutions, e. g., by Thomas and von Wicklen, *THIS JOURNAL*, **66**, 794 (1934). The introduction of this equilibrium would not greatly change the extinction coefficients of Fe^{3+} and FeOH^{2+} in Table II.

lected these changes in K_H at constant μ in the calculations of $\epsilon_{\text{Fe}^{3+}}$ and $K_H \epsilon_{\text{FeOH}^{2+}}$. The above results show that this neglect may cause appreciable errors; but without a quantitative theory of the effect, we saw no simple way to improve on our calculations. The error in the $\epsilon_{\text{Fe}^{3+}}$ values probably is small, particularly above 400 $m\mu$, since this term in (7b) is, in our experiments, always at least three times as large as the term $K_H \epsilon_{\text{FeOH}^{2+}}/[\text{H}^+]$.

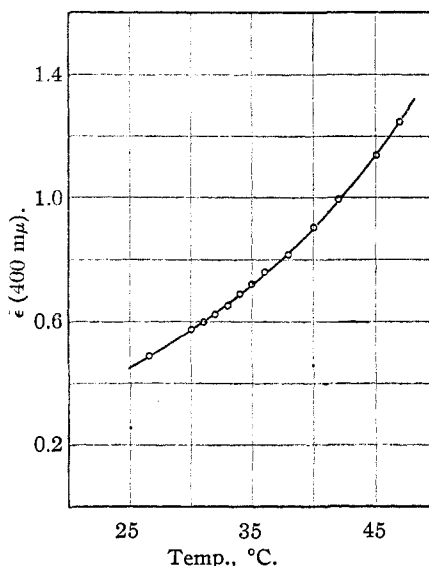


Fig. 5.—Increase in the average absorption coefficient of $\text{Fe}^{3+} + \text{FeOH}^{2+}$ at 400 $m\mu$ with temperature, due to increased hydrolysis: $[\text{Fe}(\text{ClO}_4)_3] = 0.10$ m./l.; $\mu = 1.10$; $[\text{HClO}_4] = 0.50$ m./l.

Figure 5 shows the large effect of an increase in temperature on the absorption of a ferric perchlorate solution in the region (400 $m\mu$), where $\text{Fe}(\text{OH})^{2+}$ contributes to it. (These solutions become yellow upon heating and regain the original pinkish violet color upon cooling.) This shows that the formation of FeOH^{2+} is an endothermal process. In Fig. 6 (Curve II) $\log(\bar{\epsilon} - \epsilon_{\text{Fe}^{3+}})$ of a ferric perchlorate solution is plotted against $1/T$. According to equation (7b), the slope of this line is $d \log K_H/d(1/T)$ (we can assume that $[\text{H}^+]$ is not affected by temperature). Using the thermodynamic relation $d \log K_H/d(1/T) = 2.30RT\Delta H_H$, where ΔH_H means the heat effect of reaction (5) we obtain from Fig. 6

$$\Delta H_H = 12.3 \approx 1 \text{ kcal.}$$

For comparison, the heat of hydrolysis can be calculated from the two values $K_H^0 = 6 \times 10^{-8}$ and 12×10^{-8} which Bray and Hershey⁴ gave

for 25 and 35°, respectively. The combination of these two figures gives $\Delta H_H = 12.7$ kcal., in excellent agreement with the above calculated value.

By combining ΔH_H with the value of ΔF_H^0 (which can be calculated from the equilibrium constants K_H^0 given by Lamb and Jacques³ or Bray and Hershey) the entropy of hydrolysis, ΔS_H^0 , can be estimated. We obtain in this way

$$\begin{array}{ll} K_H^0 & 6 \times 10^{-3} \text{ (B. H.) or } 3.5 \times 10^{-3} \text{ (L. J.)} \\ \Delta F_H^0 & 3.1 \text{ kcal. or } 3.4 \text{ kcal.} \\ \Delta S_H^0 & 31 \text{ e. u. or } 30 \text{ e. u.} \end{array}$$

These constants are for reaction (5). By adding the corresponding values for the neutralization reaction, we obtain the thermodynamic constants for reaction (5'), which is the association reaction proper

	ΔH , kcal.	ΔF^0 , kcal.	ΔS^0 , e. u.
$\text{Fe}^{3+} + \text{H}_2\text{O} \longrightarrow \text{FeOH}^{2+} + \text{H}^+$	12.3	3.1	31
$\text{OH}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O}$	-13.5	-19.1	19
$\text{Fe}^{3+} + \text{OH}^- \longrightarrow \text{FeOH}^{2+}$	-1.2	-16.0	50

IV. The Ions FeCl^{2+} and FeBr^{2+} . Spectra and Thermodynamic Constants

Addition of hydrochloric acid to ferric perchlorate solutions causes a change in color from the purple of Fe^{3+} ions to the yellow of the associated ions. The way in which the optical density increases with the concentration of Cl^- ions (*cf.* Figs. 10 and 11) indicates that several colored complexes are formed successively and that the successive stages of association overlap each other. The easiest way to study the first associate without interference by the higher ones is to reverse the procedure, *i. e.*, to add increasing quantities of ferric perchlorate to a solution containing a small constant amount of chloride. As soon as the total concentration of iron, $[\text{Fe}^{3+}]_0$, becomes much larger than that of the chloride, $[\text{Cl}^-]_0$, the probability of one Fe^{3+} ion being associated with more than one chloride ion becomes negligible. Under these conditions

$$[\text{Fe}^{3+}] \simeq [\text{Fe}^{3+}]_0$$

and we obtain from eq. (1)

$$[\text{FeCl}^{2+}] = \frac{K_1[\text{Cl}^-]_0[\text{Fe}^{3+}]_0}{1 + K_1[\text{Fe}^{3+}]_0} \quad (11)$$

The optical density of these solutions, $\bar{\epsilon}[\text{Fe}^{3+}]_0$ ($= 1/d \log_{10}(I_0/I)$) contains, in addition to the two terms in (7a), which represented the contribution of the Fe^{3+} ions and the FeOH^{2+} ions, a third term representing the contribution of the FeCl^{2+} ions

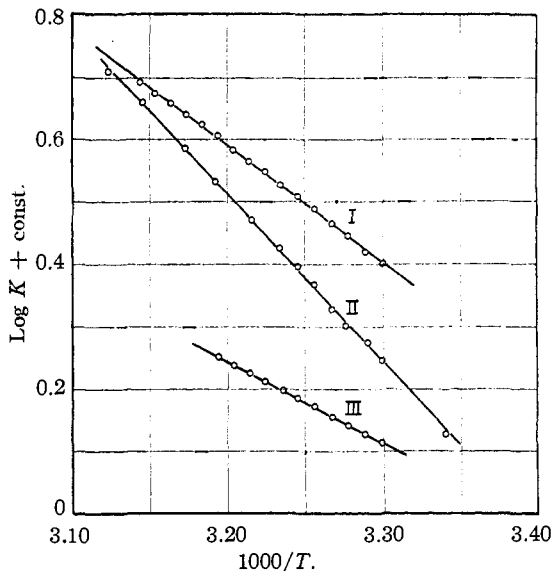


Fig. 6.— $-\log K_H$, $\log K_1$ and $\log K_{Br}$ as function of $1/T$: Curve I, for K_1 : $[\text{Fe}(\text{ClO}_4)_3] = 0.00406$ m./l., $[\text{HClO}_4] = 0.523$ m./l., $[\text{HCl}] = 0.0573$ m./l., $\mu = 0.61$; Curve II, for K_H : $[\text{Fe}(\text{ClO}_4)_3] = 0.10$ m./l., $[\text{HClO}_4] = 0.50$ m./l., $\mu = 1.10$; Curve III, for K_{Br} : $[\text{Fe}(\text{ClO}_4)_3] = 0.00413$ m./l., $[\text{HClO}_4] = 0.50$ m./l., $[\text{HBr}] = 0.065$ m./l., $\mu = 0.59$.

$$\begin{aligned} \bar{\epsilon}[\text{Fe}^{3+}]_0 &= \epsilon_{\text{Fe}^{3+}}[\text{Fe}^{3+}] + \epsilon_{\text{FeOH}^{2+}}[\text{FeOH}^{2+}] + \\ &\epsilon_{\text{FeCl}^{2+}}[\text{FeCl}^{2+}] = \epsilon_{\text{Fe}^{3+}}[\text{Fe}^{3+}]_0 + \epsilon_{\text{FeOH}^{2+}} \frac{K_H[\text{Fe}^{3+}]_0}{[\text{H}^+]} + \\ &\epsilon_{\text{FeCl}^{2+}} \frac{K_1[\text{Cl}^-]_0[\text{Fe}^{3+}]_0}{1 + K_1[\text{Fe}^{3+}]_0} \quad (12) \end{aligned}$$

The first two terms could be calculated from the curves in Fig. 2, but because of the dependence of K_H on the specific composition of the solution, described in the preceding section, it is safer to determine them empirically by comparing the absorption of each chloride solution with the absorption of a similar solution without the chloride. The difference in optical densities gives directly the FeCl^{2+} term in eq. (12).

Figure 7A shows $\epsilon_{\text{FeCl}^{2+}}[\text{FeCl}^{2+}]$ as a function of $[\text{Fe}^{3+}]_0$ for several representative wave lengths. In these experiments, $[\text{Cl}^-]_0$ was 0.002 mole/l.; since the second association constant K_2 is of the order of unity (*cf.* Section V), the ratio $[\text{FeCl}_2^+]/[\text{FeCl}^{2+}] = K_2[\text{Cl}^-]$ was < 0.002 (in presence of Fe^{3+} , $[\text{Cl}^-] < [\text{Cl}^-]_0$). Consequently, no interference by FeCl_2^+ ions needs to be considered even if these ions should be more deeply colored than the ions FeCl^{2+} .

According to eq. (12), the initial slope of each curve is $K_1\epsilon_{\text{FeCl}^{2+}}[\text{Cl}^-]_0$, and its saturation value is $\epsilon_{\text{FeCl}^{2+}}[\text{Cl}^-]_0$; since $[\text{Cl}^-]_0$ is known, these two parameters permit the calculation of K_1 and

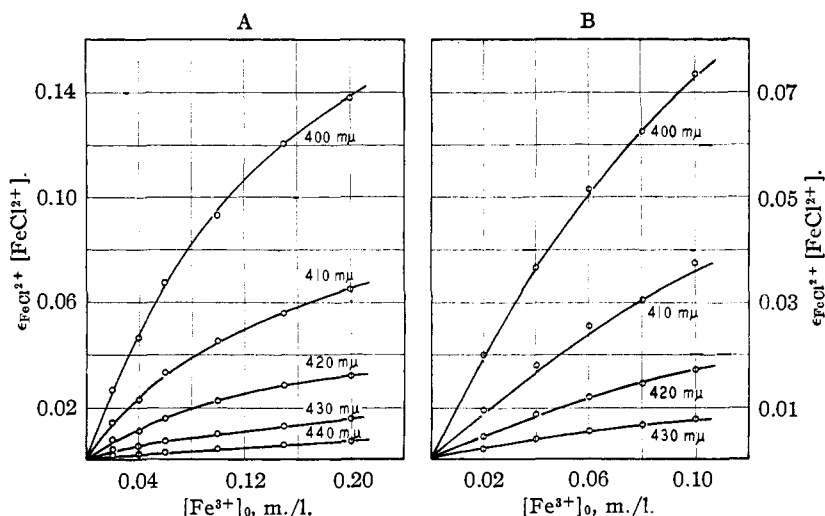


Fig. 7.—Increase in absorption of an HCl solution with the addition of $\text{Fe}(\text{ClO}_4)_3$, due to the formation of FeCl_2^{2+} ions: (A) at $\mu = 2.186$, $[\text{HCl}] = 0.002$ m./l., $[\text{HClO}_4] = 0.986$ m./l., $\text{Fe}(\text{ClO}_4)_3 = 0.02$ to 0.20 m./l., $[\text{NaClO}_4] = 1.08$ to 0 m./l.; (B) at $\mu = 1.094$, $[\text{HCl}] = 0.002$ m./l., $[\text{HClO}_4] = 0.492$ m./l., $[\text{Fe}(\text{ClO}_4)_3] = 0.01$ to 0.1 m./l., $[\text{NaClO}_4] = 0.54$ to 0 m./l.

$\epsilon_{\text{FeCl}_2^{2+}}$. The abscissa corresponding to half-saturation ($[\text{FeCl}_2^{2+}] = \frac{1}{2}[\text{Cl}^-]_0$) also can be used as a parameter: according to eq. 11, it is equal to $1/K_1$. We first fitted an equation of the type $y = ax/(1 + bx)$ to the 400 $m\mu$ curve in Fig. 7A and obtained in this way the constants $\epsilon_{\text{FeCl}_2^{2+}}^{400} = 128$ and $K_1 = 6.0$. With the same value of K_1 , the initial slopes of the other curves in Fig. 7A gave the extinction coefficients tabulated in Table II. The curves in Fig. 7A have been calculated with these constants and they fit the experimental points very well, except for a few points at the lowest $[\text{Fe}^{3+}]_0$ values. This agreement confirms that the absorption is due to the ions FeCl_2^{2+} .

When K_1 is changed, *e. g.*, by a change in μ , the ϵ values can be expected to remain unaffected. Figure 7B shows how the results obtained in a solution with $\mu = 1.094$ can be represented by curves calculated with the ϵ values from Fig. 7A with the help of only one new constant, $K_1 = 4.2$.

The absorption curve of FeCl_2^{2+} is given in Fig. 12, together with that of the other complexes.

In Fig. 8, the values of $\log K_1$, obtained from these and similar experiments, are plotted against $\sqrt{\mu}$. The association has a minimum in the region $\mu = 1$. The drawn-out curve has the equation

$$\log K_1 = +1.51 - \frac{3\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} + 0.295\mu \quad (13)$$

whose general form and limiting slope are suggested by the Debye-Hückel theory. The con-

stant term (the logarithm of association constant at infinite dilution) corresponds to $K_1^0 = 32$ (at 26.7° , which was the temperature of all these experiments), or to $K_1^0 = 30$ at 25° .

Another method of extrapolation of K_1^μ is illustrated by the dotted line, which starts with Bray and Hershey's⁴ value of $K_1^0 = 22$ ($\neq 5$) (corrected to 26.7°), and uses activity coefficients estimated by these authors. Both curves indicate a satisfactory agreement between our results and those of Bray and Hershey.⁴ This cannot be said of the value $K_1 = 1.3$ (for $\mu = 0.67$) calculated by Bent and French⁶

from spectrophotometric observations, in which FeCNS^{2+} was used as a colored "indicator" of the concentration of free Fe^{3+} ions. Bent and French⁶ neglected the higher associations, although they worked with concentration of chloride up to 0.6 mole/l., a region in which at least the ions FeCl_2^{2+} should be taken into consideration (*cf.* Fig. 13). However, this neglect cannot account for the very low K_1 value; rather it should tend to increase the

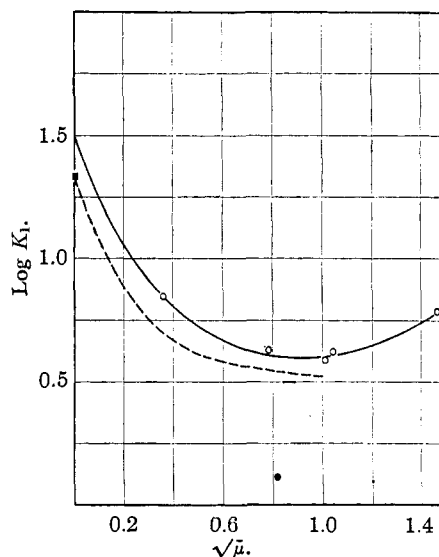


Fig. 8.—Association constant of Fe^{3+} and Cl^- as a function of ionic strength: \circ , our values; the solid curve is from equation (13); \blacksquare , Bray and Hershey; the dotted line is constructed from their activity coefficients; \bullet , Bent and French.

TABLE I

Reaction	ΔH , kcal./mole	K^0	$t = 25^\circ\text{C.}, \mu = 0$ ΔF^0	ΔS^0
$\text{Fe}^{3+} + \text{OH}^- \longrightarrow \text{FeOH}^{2+}$	-1.2 ± 1	5×10^{11a}	-16.0 ± 0.3	50 ± 4
$\text{Fe}^{3+} + \text{CNS}^- \longrightarrow \text{FeCNS}^{2+}$	960 ^b	- 4.0	...
$\text{Fe}^{3+} + \text{Cl}^- \longrightarrow \text{FeCl}^{2+}$	8.5 ± 0.2	30	-2.0 ± 0.2	35 ± 2
$\text{Fe}^{3+} + \text{Br}^- \longrightarrow \text{FeBr}^{2+}$	6.1 ± 0.2	4	-0.8 ± 0.3	23 ± 2

^a Bray and Hershey⁴; the value obtained by Lamb and Jacques³ is about one-half as large. ^b Edmonds and Birnbaum⁷; the value obtained by Bent and French⁶ is about one-fourth as large.

apparent value of this constant. Perhaps "mixed" complexes, *e. g.*, FeCNSCl^+ , played an unrecognized part in their experiments. If the color of these mixed complexes is deeper than that of FeCNS^{2+} , their presence might cause an underestimation of the quantity of Fe^{3+} ions bound by the chloride.

As in the case of FeOH^{2+} , the yellow color due to FeCl^{2+} is enhanced by an increase in temperature. Calculating K_1 for different temperatures (20 to 50°) according to eq. (13) and plotting $\log K_1$ against $1/T$, we obtain a straight line (Fig. 6, curve I) and calculate from its slope

$$\Delta H_1 = 8.5 \pm 0.2 \text{ kcal./mole}$$

for the heat of association of Fe^{3+} and Cl^- ; using the value $K_1^0 = 30$ for the association constant at 25°, we can also estimate ΔF_1^0 and ΔS_1^0 (*cf.* Table I).

The association constant of ferric ions with bromide ions is considerably smaller than that with chloride ions. Thus a series of solutions containing 0.002 m./l. of hydrobromic acid, and varying in ferric perchlorate concentration from 0.02 to 0.10 m./l., showed only small signs of saturation so that these experiments gave exact values only for the product $K_{\text{Br}} \times \epsilon_{\text{FeBr}^{2+}}$. The maximum of the FeBr^{2+} absorption band lies at about 405 m μ , where $K_{\text{Br}} \epsilon$ equals 2880 (Table II). Since 10^4 is a reasonable upper limit for the absorption coefficient at the maximum (*cf.* the curves of *v. Kiss, Abraham and Hegedüs*⁹), 0.3 should be a lower limit for K_{Br} . On the other hand, we can assume $K_{\text{Br}} < 1$, for the observed slow saturation precludes the possibility of half-saturation being reached at $[\text{Fe}^{3+}] < 1$ mole/l. The most likely value of K_{Br} for these solutions ($\mu = 1.092$) is therefore 0.5 ± 0.2 . By use of the same function employed to derive K_1^0 (see Fig. 8), we find $K_{\text{Br}}^0 = 3.8 \pm 1$, and $\Delta F_{\text{Br}}^0 = -0.8 \pm 0.2$ kcal./mole. The effect of temperature on K_{Br} is shown by curve III in Fig. 6. From the slope, we calculate the thermochemical data shown in Table I. In this table, the values of ΔH^0 , ΔF and ΔS^0

of reactions (1), (4) and (5) are compared among themselves and with ΔF^0 for the formation of the FeCNS^{2+} complex according to Edmonds and Birnbaum.⁷ The affinity of Fe^{3+} ions for OH^- ions is much larger than for the halogen ions; that for CNS^- ions a little larger. The association with OH^- ions is exothermal; that with the halogen ions endothermal. In other words, the electrostatic energy gained by the association of Fe^{3+} with the halogen anions does not compensate for the loss in hydration energy. The entropy increases in all associations are shown in Table I. It has been found in a recent paper¹⁵ that the entropy of association of *two organic cations* is *negative*. This difference in sign can be attributed to the fact that the association of two ions of opposite signs leads to a partial or complete cancellation of charges, releasing water molecules immobilized in the hydration sphere and increasing the disorder in the solution, whereas the association of two ions of like sign has no such effect on the hydration sphere and merely increases the order by binding

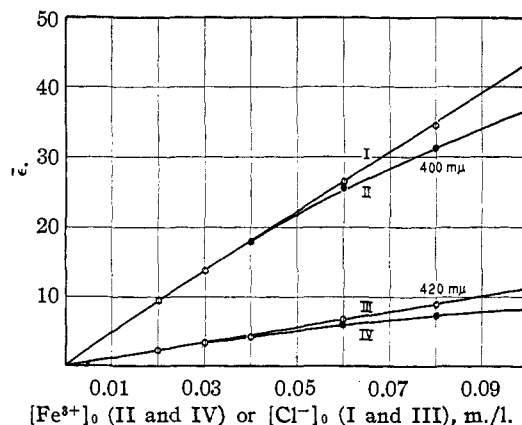


Fig. 9.—Effect of the second association step on the absorption at 400 and 420 m μ : Curves II and IV: $[\text{Fe}(\text{ClO}_4)_3] = 0.02$ to 0.1 m./l., $[\text{HClO}_4] = 0.492$ m./l., $[\text{HCl}] = 0.002$ m./l., $[\text{NaClO}_4] = 0$ to 0.48 m./l., $\mu = 1.09$ (first association only); Curves I and III: $[\text{Fe}(\text{ClO}_4)_3] = 0.002$ m./l., $[\text{HClO}_4] = 0.1$ to 0.02 m./l., $[\text{HCl}] = 0.02$ to 0.1 m./l., $\mu = 1.03$ (first and second association).

(15) E. Rabinowitch and L. F. Epstein, *THIS JOURNAL*, **63**, 69 (1941).

TABLE II
MOLAR EXTINCTION COEFFICIENTS
[$\epsilon d = \log_{10}(I_0/I)$]

λ , $m\mu$	Fe^{3+} $\epsilon \times 10^2$	$K_H \epsilon$ ($\mu = 1$)	ϵ if $K_H =$ 1×10^{-3}	FeCl^{2+} ϵ	FeCl_2^+ $K_2 \epsilon$ ($\mu = 1$)	ϵ if $K_2 = 1.3$	FeCl_3 $\epsilon \times 10^{-2}$	$K_{Br} \epsilon$ ($\mu =$ $1) \times 10^{-2}$	FeBr^{2+} $\epsilon \times 10^{-2}$ if $K_{Br} = 0.5$
400	22.5	0.102	102	128	200	155	34	28.6	57.2
407	33.4 (max.)	.063	63	28.8	57.6
410	32.6	.057	57	61	30	28.4	56.8
415	21.3	.055	55
420	11.3	.035	35	30	90	70	22	26.9	53.8
430	5.5	.020	20	13.6	16	23.4	46.8
440	4.4 (min.)	.017	17	5.8	40	30	10	19.8	39.6
450	4.6	.013	13	2.3	16.0	32
460	4.8	.011	11	5	13.0	26
470	5.5	.0065	6.5
480	6.0	.005	5	7.5	15.0
490	6.8	.002	2
500	7.5	4.0	8.0
550	9.7 (max.)	0.5	1.0
640	5.3 (min.)
700	6.2 (max.)

two previously free particles to a more or less rigid unit.

V. The Higher Associates of Fe^{3+} and Cl^- Ions

If, instead of $[\text{Cl}]_0^-$ being kept constant and $[\text{Fe}^{3+}]_0$ being increased, the latter concentration is kept constant at a low value, and $[\text{Cl}]_0^-$ gradually increased, a set of absorption curves is obtained which reflects a successive association of Fe^{3+} ions with an increasing number of Cl^- ions. We limit our considerations to the first three complexes, FeCl^{2+} , FeCl_2^+ and FeCl_3 , although there are definite indications that in concentrated chloride solutions the association proceeds further, at least to FeCl_4^- anions. An equation expressing the average absorption coefficient $\bar{\epsilon}$ ($= \log_{10}(I_0/I)/d[\text{Fe}^{3+}]_0$) of acid solutions containing small constant amounts of trivalent iron, $[\text{Fe}^{3+}]_0$ and larger variable amounts of chloride, $[\text{Cl}^-]_0$, is easily obtained from the equilibrium conditions (1), (2) and (3).

$$[\text{Fe}^{3+}]_0 = \{\epsilon_{\text{Fe}^{3+}}[\text{Fe}^{3+}] + \epsilon_{\text{FeOH}^{2+}}[\text{FeOH}^{2+}] + \epsilon_{\text{FeCl}^{2+}}[\text{FeCl}^{2+}] + \epsilon_{\text{FeCl}_2^+}[\text{FeCl}_2^+] + \epsilon_{\text{FeCl}_3}[\text{FeCl}_3]\} \quad (14)$$

$$= \frac{\bar{\epsilon}_0 + \epsilon_{\text{FeCl}^{2+}}K_1[\text{Cl}^-]_0 + \epsilon_{\text{FeCl}_2^+}K_1K_2[\text{Cl}^-]_0^2 + \epsilon_{\text{FeCl}_3}K_1K_2K_3[\text{Cl}^-]_0^3}{1 + K_1[\text{Cl}^-]_0 + K_1K_2[\text{Cl}^-]_0^2 + K_1K_2K_3[\text{Cl}^-]_0^3} \quad (14a)$$

In equation (14a), $\bar{\epsilon}_0$ means the average absorption coefficient of free ferric ions together with the FeOH^{2+} ions ($\bar{\epsilon}$ in eq. (7)), and is a function of $p\text{H}$. Since the $(\text{Fe}^{3+} + \text{Cl}^-)$ associates are much more strongly colored than free Fe^{3+} ions, and much more abundant than the $(\text{Fe}^{3+} + \text{OH}^-)$ associates, the $\bar{\epsilon}_0$ term in (14a) plays only the part of a small correction.

Equation (14a) contains seven constants: K_1 , K_2 , K_3 , $\bar{\epsilon}_0$, $\epsilon_{\text{FeCl}^{2+}}$, $\epsilon_{\text{FeCl}_2^+}$ and ϵ_{FeCl_3} . Of these, K_1 and $\epsilon_{\text{FeCl}^{2+}}$ have already been determined, and $\bar{\epsilon}_0$ is known from the results described in Section II; the four constants K_2 , K_3 , $\epsilon_{\text{FeCl}_2^+}$ and ϵ_{FeCl_3} remain disposable.

We first determine the product $\epsilon_{\text{FeCl}_2^+}K_2$ from Fig. 9, which shows $\epsilon_{\text{cor.}}$ (the subscript "cor." referring to the fact that the $\bar{\epsilon}_0$ term has been eliminated) as a function of $[\text{Fe}^{3+}]_0$, at constant $[\text{Cl}^-]_0$ ($= 0.002$ m./l.) (curves II and IV), and as a function of $[\text{Cl}^-]_0$ at constant $[\text{Fe}^{3+}]_0$ ($= 0.002$ m./l.) (curves I and III). If the association were restricted to the first step, the two curves would coincide—the first one following the equation

$$\bar{\epsilon}_{\text{cor.}} = \frac{K_1\epsilon_{\text{FeCl}_2^+}[\text{Fe}^{3+}]_0}{1 + K_1[\text{Fe}^{3+}]_0}$$

and the second one a similar equation in which $[\text{Cl}^-]_0$ replaces $[\text{Fe}^{3+}]_0$. We notice, however, that the pairs of curves in Fig. 9 diverge. The curve corresponding to constant $[\text{Cl}^-]_0$, which is unaffected by the higher complexes, falls below that corresponding to constant $[\text{Fe}^{3+}]_0$. At low $[\text{Cl}^-]_0$ values, this difference must be due

predominantly to the formation of the second complex species, FeCl_2^+ . It follows from eq. (14a) that under these conditions

$$\bar{\epsilon}_{\text{cor.}} \approx \frac{K_1[\text{Cl}^-]_0}{1 + K_1[\text{Cl}^-]_0} (\epsilon_{\text{FeCl}^{2+}} + \epsilon_{\text{FeCl}_2^+}K_2[\text{Cl}^-]_0) \quad (15)$$

In Fig. 9, the upper curve in each pair represents $\bar{\epsilon}_{\text{cor.}}$ in (15) whereas the lower represents the first term in this equation. Thus, the difference be-

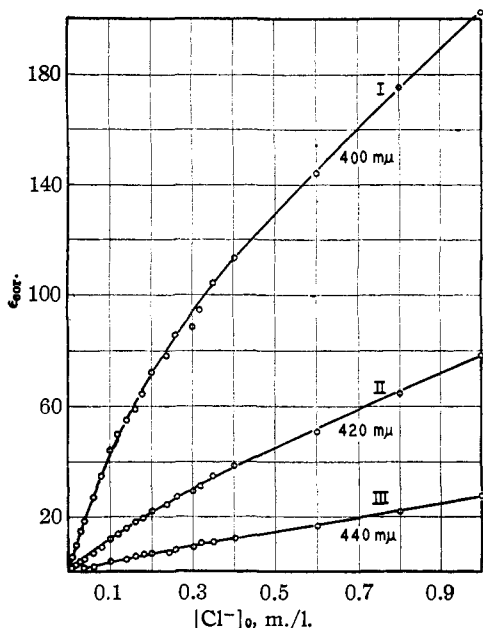


Fig. 10.—Average absorption coefficient of Fe^{3+} in HCl solutions: $[\text{Fe}(\text{ClO}_4)_3] = 0.002$ m./l.; $[\text{HClO}_4] = 0.99$ to 0 m./l.; $[\text{HCl}] = 0.01$ to 1.0 m./l.; $\mu = 1.01$. Equations of the curves ($x = [\text{Cl}^-]_0$):

$$\begin{aligned} \text{I, } \bar{\epsilon}_{\text{cor.}} &= \frac{537x + 840x^2 + 845x^3}{1 + 4.2x + 5.5x^2 + 0.3x^3} \\ \text{II, } \bar{\epsilon}_{\text{cor.}} &= \frac{126x + 378x^2 + 354x^3}{1 + 4.2x + 5.5x^2 + 0.3x^3} \\ \text{III, } \bar{\epsilon}_{\text{cor.}} &= \frac{24.3x + 168x^2 + 108x^3}{1 + 4.2x + 5.5x^2 + 0.3x^3} \end{aligned}$$

tween them gives the second term, and permits the calculation of $\epsilon_{\text{FeCl}_2} K_2$. The values of $K_2\epsilon$ in Table II were obtained in this way.

Figure 10 shows the average absorption coefficients of solutions containing 0.002 m./l. ferric perchlorate and up to 1.0 m./l. hydrochloric acid for several selected wave lengths, at a constant acidity ($[\text{H}^+] = 1$ m./l.) and constant ionic strength ($\mu = 1.03$). From the continued approximately linear increase in $\bar{\epsilon}$ in the region $[\text{Cl}^-]_0 = 0.4$ to 1.0 m./l., we conclude that in this region the "saturation" of ferric chloride is still far away; this conclusion is confirmed by experiments at the higher $[\text{Cl}^-]_0$ values (Fig. 11) which make it probable that ferric chloride is "half-saturated" only in about 5 or 6 molar hydrochloric acid. Thus, in the interpretation of the results at $[\text{Cl}^-]_0 \leq 1$ m./l., the last term in the denominator of (14a) can be omitted in the first approximation (this being the term which accounts for the "saturation" of ferric chloride), and re-introduced later as a correction determined from the first approximation value of K_3 . In the first

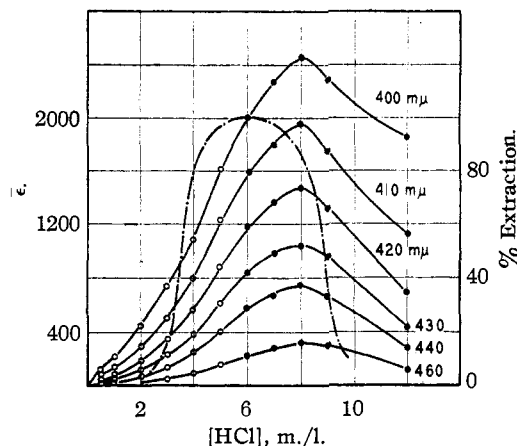


Fig. 11.—Average absorption coefficient of Fe^{3+} in HCl solutions: \circ , $[\text{Fe}(\text{ClO}_4)_3] = 0.002$ m./l., $[\text{HClO}_4] = 0.01$ m./l., $[\text{HCl}] = 0.05$ to 5 m./l.; \bullet , $[\text{Fe}(\text{ClO}_4)_3] = 0.001$ m./l., $[\text{HClO}_4] = 0.005$ m./l., $[\text{HCl}] = 6$ to 12 m./l.; — — — extractability with ethyl ether.

attempt to fit theoretical curves to the data in Fig. 10, we are thus left with only two adjustable constants: $\epsilon_{\text{FeCl}_2} \times K_3$ in the numerator of (14a), and K_2 in the denominator. We found by trial that the best fit can be obtained by means of the value

$$K_2 = 1.3 \quad (\mu = 1)$$

and of the $\epsilon_{\text{FeCl}_2} K_3$ values of 153 at 400 $m\mu$ and 64 at 420 $m\mu$. Table II contains the values of ϵ_{FeCl_2} calculated from the products $K_2\epsilon$ by means of the above value of K_2 .

It now remains to split the product $\epsilon_{\text{FeCl}_2} K_3$ into its two factors. Figure 11 shows $\bar{\epsilon}$ of chloride solutions at hydrochloric acid concentrations up to 12 m./l. plotted against $[\text{Cl}^-]_0$. (No attempt was made to maintain a constant ionic strength in these experiments.) The curves in Figure 11 show the "saturation" of ferric chloride to become manifest in the region $[\text{Cl}^-]_0 = 5$ to 8; at still higher $[\text{Cl}^-]_0$ values, the optical density decreases again. This indicates the formation of higher associates beginning with FeCl_4^- , which apparently are less intensely colored than the ferric chloride molecules, at least as far as absorption in the region 400–460 $m\mu$ is concerned. These results are in qualitative agreement with the absorption curves which v. Kiss and co-workers⁹ have obtained in 10.0 and 12.47 molar hydrochloric acid and according to which the absorption in the region 390–590 $m\mu$ is weaker in the more concentrated hydrochloric acid solution (the relation is reversed in the ultraviolet and in the red).

The curves in Fig. 11 permit a rough graphical

extrapolation of ϵ_{FeCl_3} as the limiting values which the curves would approach if their direction were not reversed by the formation of the higher associates. The values shown in Table II were obtained in this way. Combining these values of ϵ_{FeCl_3} with the above-estimated values of $K_3\epsilon_{\text{FeCl}_3}$, we obtain

$$K_3 = 0.04 \pm 0.02 \quad (\mu = 1.03)$$

According to this K_3 value, ferric chloride must be "half-saturated" at $[\text{Cl}_0^-] = 20$ m./l. However, this K_3 value corresponds to $\mu = 1$, an ionic strength incompatible with the required concentration of Cl^- ions. To a very rough approximation, we can expect that at other ionic strengths ferric chloride will be half-saturated when the activity of hydrochloric acid is $a_{\text{HCl}} = 20$, *i. e.*, according to Åkerlöf and Teare,¹⁶ in approximately 6.5 molar hydrochloric acid. This expectation is confirmed by Fig. 11. We now have evaluated all constants in (14a); the solid lines in Fig. 10 show how closely the experimental points fall on the theoretical curves calculated from equation (14a) by means of these constants.

Figure 12 shows the absorption curves of Fe^{3+} , FeCl^{2+} , FeCl_2^+ and FeCl_3 in a semi-logarithmic diagram. It indicates that all three associate species are yellow. It is obvious from the preceding discussion that the data for FeCl_2^+ and FeCl_3 are only in the nature of rough estimates.

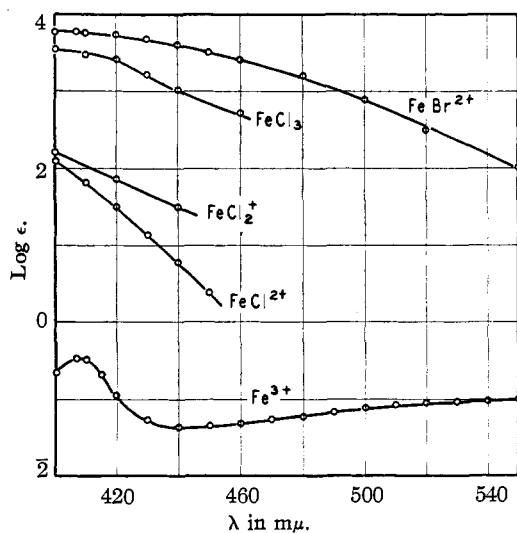


Fig. 12.—Absorption curves of ferric ion and its halogen complexes in the visible region.

The same remark applies to the values of the three successive association constants

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

$$\begin{array}{ll} \mu = 1, t = 26.7^\circ & \mu = 0, t = 25^\circ \\ K_1 = 4.2 \pm 0.2 & K_1^0 = 30 \pm 5 \\ K_2 = 1.3 \pm 0.4 & K_2^0 = 4.5 \pm 2 \\ K_3 = 0.04 \pm 0.02 & K_3^0 = 0.1 \pm 0.05 \end{array}$$

of which the first can be considered as fairly exact, and the other two only as estimates. Figure 13 shows the distribution of Fe^{3+} between different ionic species, at $\mu = 1$, for $[\text{Cl}^-]$ values up to 1 m./l., calculated on the basis of these constants.

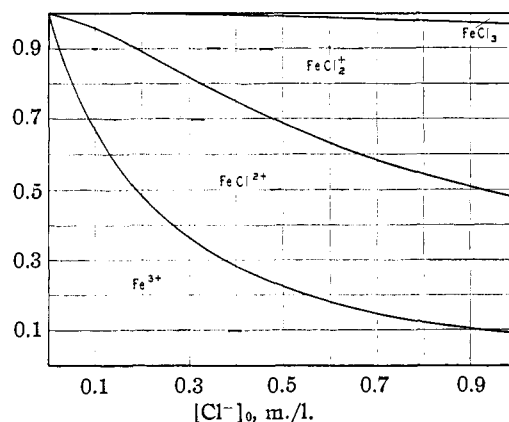


Fig. 13.—Approximate composition of ferric ion solutions at different concentration of HCl (up to 1 mole/l.), for $\mu = 1$.

Although the results are very approximate, it is certain that the first two constants K_1 and K_2 have the same order of magnitude. This behavior contrasts with that of the $\text{Fe}^{3+} + \text{OH}^-$ complexes according to Lamb and Jacques,³ which have widely spaced equilibrium constants.

$$\begin{array}{lll} K_{\text{H}_1}^0 & K_{\text{H}_2}^0 & K_{\text{H}_3}^0 \\ 350 \times 10^{-5} & 2 \times 10^{-5} & 0.04 \times 10^{-5} \end{array}$$

This difference may be due to the more purely ionic binding in the complex chloride as compared with the complex hydroxides. In particular the binding of the first and of the second Cl^- ion on two diametrically opposite sides of a Fe^{3+} ion may be expected to yield almost equal amounts of energy, so that the difference between the first and the second association constant can be ascribed mainly to the different statistical probabilities. If we assume that Cl^- replaces one of the six water molecules in the hydration sphere of the Fe^{3+} ion, then the first Cl^- can choose any one of the six, whereas the second one has no choice, since it must replace the water molecule diametrically opposite to the first Cl^- ion (this position corresponding to the minimum electrostatic energy). Thus, the "statistical" factor in

the ratio $K_1:K_2$ should be 6. The observed ratio is about 3.3 at $\mu = 1$, corresponding to about 6.8 at $\mu = 0$. (The difference between the last two values is due to the fact that the factors in the function of Bray and Hershey⁴ by means of which K_2 was extrapolated to $\mu = 0$, depend on the valencies of the associating ions.)

The interpretation of the absorption maximum in Fig. 11 as corresponding to the maximum concentration of ferric chloride finds a strong support in the results of Dodson, Forney and Swift¹⁷ on the effect of hydrochloric acid concentration on the extractability of ferric chloride solutions by ethers, which show, for different ethers, maxima between 6 and 8 m./l. (*cf.* dotted line in Fig. 11). The extreme sharpness of this maximum, as well as the fact that the relative quantity of extracted ferric chloride increases with increasing concentration of iron, seems to indicate that FeCl_3 , passes into the ether in the form of associated molecules, *e. g.*, Fe_2Cl_6 . However, this conclusion contradicts the results of the molecular weight determinations of ferric chloride in organic solvents (*cf.* Gmelin's Handbook¹⁸); on the other hand, it agrees with the results of Schlesinger and van Valkenburgh¹⁹ concerning the dimerization of $\text{Fe}(\text{CNS})_3$ in ether solutions. Spectrophotometric measurements on ferric salt solutions in organic solvents would be of considerable interest in connection with this problem.

(17) R. W. Dodson, G. J. Forney and E. H. Swift, *THIS JOURNAL*, **53**, 2573 (1936).

(18) Gmelin, "Handbuch der anorganischen Chemie," 8th edition, No. 59B, p. 229.

(19) H. I. Schlesinger and H. B. van Valkenburgh, *THIS JOURNAL*, **53**, 1212 (1931).

Summary

1. Absorption curves have been determined for ferric perchlorate solutions in the presence of different amounts of OH^- , Cl^- and Br^- ions, at different temperatures and ionic strengths.

2. The absorption curves of ferric perchlorate + perchloric acid systems have been analyzed and the absorption curve of free (hydrated) Fe^{3+} ions separated from that of $\text{Fe}(\text{OH})^{2+}$ ions (Fig. 2).

3. By a similar procedure, the absorption curves of solutions containing hydrochloric acid or hydrobromic acid have been analyzed. They show several successive association steps. The absorption curves of FeCl^{2+} , FeCl_2^+ and FeCl_3 , as well as of FeBr^{2+} , have been derived (Fig. 11). All these species are yellow, ferric chloride being the most intensely colored. The complex anions ($\text{FeCl}_4^- \dots$) are only formed in very concentrated chloride solutions and are less strongly colored than ferric chloride.

4. The equilibrium constants $K_1 = 4.2$, $K_2 = 1.3$, $K_3 = 0.04$, $K_{\text{Br}} = 0.5$ (all for $\mu = 1$) of the formation of FeCl^{2+} , FeCl_2^+ , FeCl_3 and FeBr^{2+} , have been derived from the effects of changes in the concentrations of Fe^{3+} , Cl^- and Br^- on the spectra; the distribution of Fe^{III} between the several ionic species at different chloride concentrations has been calculated (Fig. 13).

5. The effect of heating on the absorption curves has been measured and the heats and entropies of formation of FeOH^{2+} , FeCl^{2+} and FeBr^{2+} determined (Table I).

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A New Method for Determining DinERIC Distribution¹

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The primary object of the present investigation was to develop a perfectly general and convenient method for determining the composition of conjugate phases in systems of three liquid components containing two immiscible or slightly miscible components, each of which is consolute with the third liquid. The method to be described is essentially graphical. It is superior to that of

chemical analysis in cases where this is tedious or unreliable, and seems to us more convenient than the refractive index schemes which have been used by some workers.

Another object of this work was to show that our distribution data for the systems investigated could be generalized by simple empirical equations; these systems were benzene-alcohol-water and chloroform-acetone-water. This matter will be discussed later in detail, and we shall

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