TABLE IV

VARIATION OF THE PARTIAL MOLAL ENTROPY OF NTA CHELATES WITH THE TRIPOSITIVE RARE EARTH METAL ION COMPLEXED

Ion	$\Delta S°_1 + \bar{S}°_{Ln}{}^a$	$\Delta S°_1 + \Delta S°_2 + \bar{S}°_{Ln}{}^b$
Y	15	42
La	20	45
Ce	18	43
Pr	15	40
Nd	15	41
Sm	14	40
Eu	15	40
Gd	14	37
Tb	16	42
Dy	18	42
Ho	19	44
Er	18	48
Tm	16	51
Yb	17	53
Lu	16	56

^{a} Estimated uncertainty $\pm$ 2 e.u. ^{b} Estimated uncertainty ± 3 e.u.

urements, and the concentration values thus reflect the same trends as the thermodynamic ones would. In comparing ΔH and $\Delta S°$ data for formation of the 1:1 and 1:2 chelates, effects due to the NTA$^-$ group can be neglected since this group is common to the formation of both. However, for the 1:1 chelate a cation (Ln^{3+}) is converted to a neutral species, whereas for the 1:2 chelate, a neutral species is converted to an anion. This amounts to removal and addition of charge, respectively. If ion–water dipole interactions are important in these systems, it is then reasonable that ΔH_1 is always more positive than ΔH_2 and that $\Delta S°_1$ is always larger than $\Delta S°_2$.

Thermodynamics of Association of Iron(III) Ion and Chloride Ion in Aqueous Solution[1]

BY SISTER M. JOHN MARK WOODS, O. P., PATRICK K. GALLAGHER, AND EDWARD L. KING

Electromotive force, spectrophotometric, and calorimetric measurements have allowed evaluation of certain thermodynamic quantities for the reaction $Fe^{+3} + Cl^- = FeCl^{+2}$. Electromotive force measurements and spectral data at 335 mμ, an absorption maximum for monochloroiron(III) ion, give values of $Q_1° = [FeCl^{+2}]/[Fe^{+3}][Cl^-]$ for a solvent of 1.0 M perchloric acid at 25° which agree well, 2.89 and 2.95 $\pm$ 0.09, respectively. Values of $\Delta H_1°$, obtained from the temperature coefficient $Q_1°$ for 1.0 M perchloric acid are +4.4 kcal./mole from electromotive force measurements and +4.1 kcal./mole from spectrophotometric measurements. The calorimetric study gave a value of $\Delta H_1° = 4.2$ kcal./mole for 1.0 M perchloric acid. The value of $\Delta S_1°$ derived from these quantities pertaining to 1.0 M perchloric acid is +16.6 cal. mole^{-1} deg.$^{-1}$, and electromotive force and calorimetric measurements yield a value of +16.1 cal. mole^{-1} deg.$^{-1}$, for $\Delta S_1°$ in 3.7 M perchloric acid as the medium; this value agrees closely with that for the analogous chromium(III)-chloride reaction, which suggests that iron(III) does not change coördination number in the reaction under consideration. Consideration has been given to medium effects which may accompany the concentration changes necessary in this study of a system showing slight association. In arriving at the conclusions stated in this summary, certain assumptions were necessary; these are given mild support by the general agreement of values obtained using the different experimental methods.

That the interaction of iron(III) ion and chloride ion is not simply an ion-atmosphere effect

is indicated by the magnitude of the second-order rate constant for the spectral change which occurs when solutions containing iron(III) ion and chloride ion are brought together.[2] Readjustment of the ion-atmosphere around iron(III) ion occurring in chloride-containing media would

(1) This work, presented in part at the 136th National Meeting of the American Chemical Society at Atlantic City, New Jersey, September 1959, is based upon Ph.D. theses of Sr. M. J. M. Woods, O.P., 1960 (electromotive force and spectrophotometric studies), and Patrick K. Gallagher, 1959 (calorimetric studies). The work was supported by the United States Atomic Energy Commission (Contract AT (11-1)-64, Project 3) and the Research Committee of the Graduate School, University of Wisconsin.

(2) R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959); see also H. Wendt and H. Strehlow, *Z. Elektrochem.*, **64**, 131 (1960).

be expected to occur more rapidly[3] than corresponds to the value 9.4 l. mole^{-1} sec.$^{-1}$ observed for $\{[Fe^{3+}][Cl^-]\}^{-1} \times d[FeCl^{2+}]/dt$ at 25°.[2] The spectral change which occurs when chloride ion is added to an acidic solution of iron(III) perchlorate, the appearance of a new peak at $\sim$335 mμ,[4,5] also suggests a new species in chloride solutions.[6] In addition to inner-sphere iron(III)–chloride species, outer-sphere interactions merging into ion-atmosphere effects undoubtedly differ in solutions containing chloride ion and in solutions containing perchlorate ion.

The principal discrepancy calling attention to need for additional study of the reaction

$$Fe^{+3} + Cl^- = FeCl^{+2} \quad \text{(Reaction 1)}$$
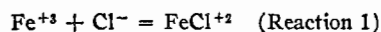
was the large difference between $\Delta S_1° = 35$ cal. mole^{-1} deg.$^{-1}$ obtained by Rabinowitch and Stockmayer,[7] and the value for the corresponding chromium(III)–chloride reaction, $\Delta S_1° = 17$ cal. mole^{-1} deg.$^{-1}$, obtained by Gates and King.[8] The value for the iron reaction was obtained from the equilibrium quotient extrapolated to zero ionic strength coupled with a value of ΔH obtained from the temperature coefficient of the absorbancy in the range 400–440 mμ measured on a solution of $I = 0.61 \ M$; the value for the chromium reaction was obtained from appropriate extrapolation of experimentally determined quantities to a medium of 4.4 molal perchloric acid. Although difference in electrolyte concentration might account for part of this discrepancy, the possibility that it was real, suggesting that a change in coördination number occurs in the iron(III) reaction, could not be dismissed. A change in coördination number does occur in one or more iron(III)–chloride complex ion reactions. Convincing arguments have been presented by Friedman[9] for iron(III) having coördination number four in tetrachloroiron(III) ion present in iron(III) solutions in concentrated hydrochloric acid, and Standley and Kruh[10] have interpreted X-ray

diffraction studies of iron(III)–chloride in hydrochloric acid solution in terms of tetrahedral tetrachloroiron(III) ion. If the coördination number change occurs in reaction 1, liberation of two extra water molecules compared to the chromium(III) reaction[11] would be expected to give an abnormally positive entropy change.[12] The present study does not, however, confirm the value of $\Delta S_1°$ suggested by Rabinowitch and Stockmayer.[7] The value obtained in the present study is close to that for the chromium(III)–chloride reaction, and we conclude that no change in coördination number occurs in reaction 1.

The present paper reports results of electromotive force, spectrophotometric, and calorimetric measurements designed to obtain values of thermodynamic quantities associated with reaction 1.

Since the equilibrium constant for reaction 1 at zero ionic strength probably is in the range 20–30,[13] difficulties of distinguishing specific association from ion-atmosphere effects, discussed by Redlich[6] and by Young and Jones,[14] are present in any study of this labile system. A calculation illustrating the situation is summarized in Figure 1. The question posed is this: What effect upon the concentration dependence of the mean stoichiometric activity coefficient of a trivalent metal chloride would result from occurrence of a reaction analogous to reaction 1 with $K_1° = 30$ if the activity coefficient of each ionic species f_i is related to the mean stoichiometric activity coefficient of sodium chloride at the same ionic strength by

$$f_i = (\gamma_\pm)_{NaCl}^{Z_i^2}$$

where Z_i is the charge of the species? This calculation shows that ion association of this magnitude has no more effect upon the stoichiometric activity coefficient of a 3–1 electrolyte than the variation expected in electrolytes considered to be completely dissociated.

(3) M. Eigen, G. Kurtze, and K. Tamm, *Z. Elektrochem.*, **57**, 103 (1953); M. Eigen, *Discussions Faraday Soc.*, **17**, 194 (1954); M. Eigen, *Z. Elektrochem.*, **64**, 114 (1960).

(4) H. Olerup, *Svensk Kem. Tidskr.*, **55**, 324 (1943); Thesis, Lund (1944).

(5) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi, and T. Kitagawa, *Bull. Chem. Soc. Japan*, **30**, 433 (1957).

(6) O. Redlich, *Chem. Revs.*, **39**, 333 (1946).

(7) E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942).

(8) (a) H. S. Gates and E. L. King, *ibid.*, **80**, 5011 (1958); (b) K. Schug and E. L. King, *ibid.*, **80**, 1089 (1958).

(9) H. Friedman, *ibid.*, **74**, 5 (1952).

(10) C. L. Standley and R. F. Kruh, *J. Chem. Phys.*, **34**, 1450 (1961).

(11) It is relatively certain that the coördination number of chromium(III) is six in chromium(III)–chloride complex species. Isomeric dichlorochromium(III) species have been isolated (E. L. King, Sr. M. J. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958)). This would not be possible if dichlorochromium(III) ion was tetrahedral $Cr(OH_2)_2Cl_2^+$.

(12) (a) P. K. Gallagher and E. L. King, *J. Am. Chem. Soc.*, **82**, 3510 (1960); (b) J. O. Edwards and R. J. Senderstrom, *J. Phys. Chem.*, **65**, 862 (1961).

(13) Nine different studies pertaining to aqueous solutions and relevant to the value of Q_1 and $K_1°$ are cited in J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, "Stability Constants of Metal Ion Complexes, Part II: Inorganic Ligands," Special Publication No. 7, The Chemical Society, London, 1958, p. 97.

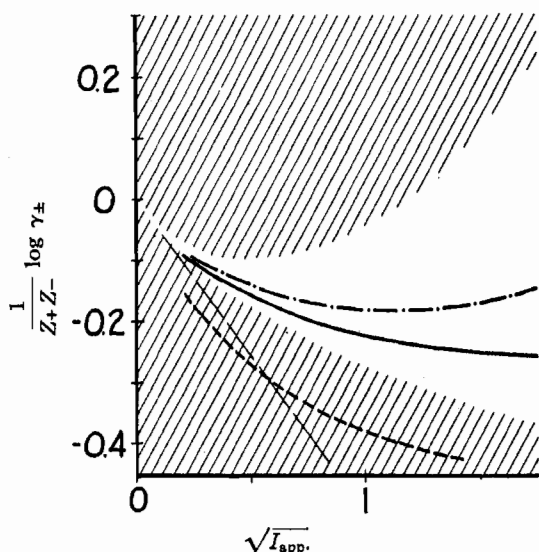(14) T. F. Young and A. C. Jones, *Ann. Revs. Phys. Chem.*, **3**, 275 (1952).

Fig. 1.—The mean stoichiometric activity coefficient of an electrolyte MCl_3 in solutions in which association occurs: $M^{+3} + Cl^- = MCl^{+2}$; $K° = 30$. It is assumed that in the absence of association, activity coefficients of all ions are given by $f_i = (\gamma_\pm)_{NaCl}{}^{Z_i{}^2}$ where Z_i is the charge on the ionic species. The mean stoichiometric activity coefficient of sodium chloride at 25° is shown by —·—·—·—·. The curve of interest $(\gamma_\pm)_{MCl_3}{}^{1/4}$ is shown by ————. In the unshaded region lie the activity coefficients of all alkali metal halides and perchlorates. There also is shown the Debye-Hückel limiting law and the square root of the mean stoichiometric activity coefficient of sulfuric acid (— — — —), in solutions of which association occurs: $H^+ + SO_4^- = HSO_4^-$; $K° = 85$. The abscissa $\sqrt{I_{app}}$ is the square root of the ionic strength which the solution would have if dissociation were complete.

The present study also is complicated by other interactions which may be of comparable magnitude to that of iron(III) ion and chloride ion. Spectrophotometric and calorimetric experiments were carried out in solutions containing hydrogen ion, iron(III) ion, chloride ion, and perchlorate ion; solutions studied in electromotive force experiments necessarily contained iron(II) ion in addition. Although values for equilibrium constants for reactions forming an iron(III)–perchlorate species[15] and an iron(II)–chloride species[4] have been presented, there is not clear evidence that it is appropriate to describe these interactions in terms of the formation of new species. In the present paper, only the interaction of iron(III) ion and chloride ion is accounted for with a chemical reaction (reaction 1); other specific interaction of ions of unlike charge is taken into account by appropriate terms in an

equation for the activity coefficient of an ion.[16] For chloride ion, the equation is

$$\log f_4 = (\text{function of } I) + b_{34}[Fe^{+3}] + b_{54}[Fe^{+2}] + b_{14}[H^+] + b_{74}[FeCl^{+2}] \quad (1)$$

in which numbers in subscripts refer to particular species: 1—H^+, 2—ClO_4^-, 3—Fe^{+3}, 4—Cl^-, 5—Fe^{+2}, and 7—$FeCl^{+2}$. (These numbers will have this significance throughout the paper.) The coefficient of $[Fe^{+2}]$, b_{54}, is related, therefore, to the influence of interaction of iron(II) ion and chloride ion upon the activity coefficient of chloride ion.

Consequences of a dependence of (a) the liquid junction potential, (b) the absorbancy index of a species, (c) the heat of dilution of an electrolyte, and (d) the heat of reaction 1 upon the composition of the medium at constant ionic strength have been investigated. Allowing for such medium effects makes it impossible to obtain unambiguous values of thermodynamic quantities pertaining to reaction 1. One can, however, make simplifying assumptions. Agreement of provisional values of the equilibrium quotient and enthalpy change for reaction 1 obtained by the several experimental methods suggests the probable validity of the assumptions used.

Experimental Details and Results

Reagents.—All solutions were prepared using doubly distilled water, the second distillation being from alkaline permanganate solution using a Barnstead still.

Reagent grade chemicals were used without further purification, except as noted.

For electromotive force measurements, solutions containing iron(II) and iron(III) perchlorate in perchloric acid were prepared by dissolving reagent grade iron wire in 0.5–0.6 M perchloric acid or by using iron(II) perchlorate (G. F. Smith Chemical Co.) which was recrystallized twice; iron(II) was partially oxidized to iron(III) with hydrogen peroxide. These solutions were shown to contain negligible amounts of chloride ion by titration with silver nitrate.

For spectrophotometric measurements, iron(III) perchlorate was prepared by evaporation of perchloric acid solutions of reagent grade iron(III) nitrate to near dryness. The salt prepared in this way was recrystallized from perchloric acid and dissolved in 1.00 M perchloric acid.

For calorimetric measurements, three iron(III) perchlorate–perchloric acid stock solutions, designated as A, B, and C, were prepared: A. Reagent grade iron wire was dissolved in excess perchloric acid; iron(II) so formed was oxidized with hydrogen peroxide, the excess being decomposed by heating the solution to boiling. Chloride ion was formed in this preparation. The composition of solution A was 2.00, M iron(III), 0.58 M hydrogen ion,

(15) K. W. Sykes, *J. Chem. Soc.*, 2473 (1959); D. H. Richards and K. W. Sykes, *ibid.*, 3626 (1960).

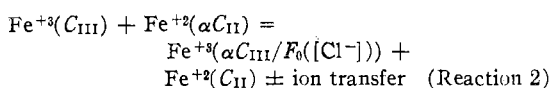(16) E. A. Guggenheim, *Phil. Mag.*, **19**, 588 (1935).

0.182 M chloride ion, and (by difference) 6.41 M perchlorate ion. B. Iron(III) perchlorate was crystallized from a solution containing perchloric acid, hydrogen peroxide, and iron(II) perchlorate (G. F. Smith Chemical Co.). The composition of solution B was 1.058 M iron(III), 1.56 M hydrogen ion, and (by difference) 4.73 M perchlorate ion. C. Reagent grade iron(III) nitrate was evaporated to near dryness with concentrated perchloric acid several times. The resulting iron(III) perchlorate was recrystallized from perchloric acid. The composition of solution C was 0.565 M iron(III), 0.894 M hydrogen ion, and (by difference) 2.59 M perchlorate ion. Negative tests for chloride ion and iron(II) were obtained upon treatment of separate portions of solutions B and C with concentrated silver nitrate and potassium ferricyanide.

Electromotive Force Measurements.—The apparatus consisted of a pair of half-cells equipped with shiny platinum electrodes containing iron(II) perchlorate, iron(III) perchlorate, and perchloric acid; into one half-cell a hydrochloric acid solution was titrated. The ionic strength was the same in each half-cell throughout a titration if changes due to occurrence of reaction 1 were not taken into account. In experiments with iron(II) and iron(III) present in the titrating solution at the same concentration as in the original solution, the hydrogen ion concentration remained constant during the titration. In other experiments the hydrogen ion concentration increased slightly during the titration. In some experiments chloride was added to one half-cell as weighed portions of potassium chloride. If the solubility of potassium perchlorate were negligible, this would be an ideal procedure. Particularly at the lower concentrations of perchloric acid, the solubility of potassium perchlorate is appreciable[17] and the ionic strength did not, therefore, remain constant during such a titration.

A Rubicon Type B Potentiometer in conjunction with a standard saturated Weston cell (Eppley Laboratory, Inc.) and a Leeds and Northrup (Type E) D. C. galvanometer, No. 2430, were used. Measurements were made to 0.01 mv.; the readings were, however, generally steady to only ~0.05 mv.; in duplicate runs the average difference of readings at supposedly identical points was ~0.3 mv. (A significant contribution to this uncertainty was the buret reading; readings which did not correspond to exactly the same composition of solution were, in fact, being compared.)

Contact between solutions in the half-cells was made through a closed ungreased ground glass joint wet with solution present in the half-cell containing no chloride ion.

The reaction occurring with passage of one faraday of current is

$$Fe^{+3}(C_{III}) + Fe^{+2}(\alpha C_{II}) =$$
$$Fe^{+3}(\alpha C_{III}/F_0([Cl^-])) +$$
$$Fe^{+2}(C_{II}) \pm \text{ion transfer} \quad \text{(Reaction 2)}$$

in which C_{II} and C_{III} are the initial concentrations of iron(II) and iron(III), respectively, α is a factor which takes into account dilution in titrations in which iron(II) and iron(III) were absent from the titrating solution, and $F_0([Cl^-])$ is equal to $\{C_{III}/[Fe^{+3}]\}$. The electromotive force of the cell is, therefore

$$E = \frac{2.3\,RT}{F} \log \left\{ F_0([Cl^-]) \times \frac{f_3 \cdot f_{6Cl}}{f_{3Cl} \cdot f_6} \right\} + E_L \quad (2)$$

in which E_L is the liquid junction potential and the subscript Cl refers to the half-cell containing chloride. The function $F_0([Cl^-])$ contains the equilibrium quotient for reaction 1, equilibrium quotients for formation of higher complexes, and quotients of activity coefficients which may vary in solutions of constant ionic strength but varying composition. The concentration of iron(III) was low enough that the concentration of uncombined chloride ion was essentially equal to the stoichiometric concentration of hydrochloric acid.

Experiments were run at $25.0 \pm 0.2°$ at $I \times$ (1. moles^{-1}) = 0.10, 0.30, 0.50, 0.70, 0.90, 1.0, 1.2, 1.4, 1.6, 2.0, 3.0, and 3.7; at $I = 1.0$ M, measurements also were made at 14.3, 16.3, 30.1, 35.4, and 44.3°.

Based upon the equilibrium quotient values presented by Milburn and Vosburgh,[18] dimeric $Fe_2(OH)_2^{+4}$ was present to an extent generally much less than 0.1% in solutions studied at 25°. The extent of acid dissociation of aquo-iron(III) ion at 25° was less than 1% except at $I = 0.1$ M; at $I = 1.0$ M, the extent was ~0.16%. Since the concentration of hydrogen ion was essentially the same in the half-cells, the slight extent of acid dissociation of aquoiron(III) ion need not be taken into account.

In all experiments, observed values of electromotive force E, corrected for the initial value, depended upon the concentration of chloride ion according to

$$\{10^{FE/2.3RT} - 1\}/[Cl^-] = a + b[Cl^-] \quad (3)$$

The initial value, taken with identical solutions present in the half-cells, should be 0.00 mv. Forty-one observed values were distributed: $\leq$ 0.01 mv., 8; between 0.02 and 0.10 mv., 14; and between 0.11 and 0.30 mv., 15. Of the four experiments with initial values greater than 0.3 mv., two were at 14.3 and 16.3°, at which temperatures the cell was somewhat sluggish, and one was at iron(II) and iron(III) concentrations of ~4 $\times$ 10^{-4} M, approximately one tenth as large as in most experiments.

Results of these experiments are summarized in Table I.

Spectrophotometric Measurements.—A Cary Model 14 spectrophotometer equipped with a thermostated cell holder was used. Measurements at 25.0, 35.0, and 45.0° were made on solutions of $I = 1.0$ M, $C_{III} = 1.48 \times 10^{-4}$ M, $[H^+] = 1.00$ M, and $[Cl^-] = 0.00, 0.20, 0.40, 0.60, 0.80,$ and 0.95 M. The wave length region studied was 400 to 200 mμ, 5-cm. cells being used at $\lambda > 300$ mμ and 2-cm. cells being used at $\lambda < 350$ mμ. The absorbancy at each wave length was consistent with the two-parameter equation[19]

$$\frac{(\bar{a} - a_0)}{[Cl^-]} = -\bar{a}\,r + r\,s \quad (4)$$

in which $\bar{a} = (\log I_0/I)/(C_{III} \cdot b)$, b is the cell length, a_0 is the value of $\bar{a}$ at $[Cl^-] = 0$, and r and s are adjustable parameters. In Table II are given values of r and s for selected wave lengths at which $\bar{a}$ varies by 25% or more in going from $[Cl^-] = 0.00$ to 0.95 M. Absorbancy

(17) R. G. Thin and A. C. Cumming, *J. Chem. Soc.*, 361 (1915).

(18) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955); see also B. O. A. Hedstrom, *Arkiv Kemi*, **6**, 1 (1953).

(19) (a) T. W. Newton and G. M. Arcand, *J. Am. Chem. Soc.*, **75**, 2449 (1953); (b) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **61**, 934 (1957).

TABLE I

THE DEPENDENCE OF ELECTROMOTIVE FORCE UPON THE CONCENTRATION OF CHLORIDE ION

$$\{10^{FE/2.3RT} - 1\}/[Cl^-] = a + b[Cl^-]$$

Experiments at 25.0 ± 0.2°

$I \times$ (l. mole^{-1})	No. of independent titrations	a	b	No. of points	Av. dev. (in mv.)[j]
0.10	4[a]	7.28	10.3	23	0.03
	2[b,h]	7.69	−27.5	15	.18
	1[b,h]	7.35	−25.7	6	.03
.30	3[a]	3.75	0.58	18	.05
.50	3[a]	3.16	0.08	25	.08
.70	2[c,g]	2.96	−0.03	14	.06
.90	2[c,g]	2.91_5	0.19	9	.20
1.00	1[b]	2.85	0.14	14	.08
	2[a]	2.91	−0.18	20	.07
	1[a,h]	2.86	0.03_5	9	.06
	1[d]	2.90	0.04_6	17	.07
	1[e,h]	2.84	−0.11	11	.04
	1[f,h]	2.74	−0.06	13	.07
1.20	1[a,g]	3.01	0.012	5	.05
1.40	1[a,g]	3.09	0.13	5	.02
1.60	2[a,g]	3.28	0.18	9	.20
2.00	1[c,g]	3.86	0.27	5	.18
3.00	2[a]	6.6	0.44	10	.38
3.72	3[a]	10.7	1.9	22	.41

Experiments at $I = 1.0\ M$ at temperatures other than 25°

T	No. of independent titrations	a	b	No. of points	Av. dev. (in mv.)[j]
14.3	4[i,h]	2.31	−0.20	21	0.22
16.3	1[c]	2.28	+0.024	4	.05
30.1	3[a]	3.12	+0.05	30	.24
35.4	2[a]	3.72	−0.26	18	.23
	1[d]	3.78	−0.08	11	.07
44.3	1[a]	4.83	−0.22	5	.10

[a] $C_{III} \cong C_{II} \cong 2.5 \times 10^{-3}\ M.$ [b] $C_{III} \cong C_{II} \cong 5 \times 10^{-4}\ M.$ [c] $C_{III} = 2.8 \times 10^{-3}\ M;$ $C_{II} = 3.8 \times 10^{-3}\ M.$ [d] $C_{III} \cong C_{II} \cong 5 \times 10^{-3}\ M.$ [e] $C_{III} \cong C_{II} \cong 1.1 \times 10^{-2}\ M;$ in this run, it was necessary to correct the stoichiometric concentration of chloride ion for that tied up by iron(III) to obtain the true concentration of chloride ion. [f] $C_{III} \cong C_{II} \cong 2.3 \times 10^{-2}\ M;$ in this run, it was necessary to correct the stoichiometric concentration of chloride ion for that tied up by iron(III) to obtain the true concentration of chloride ion. [g] Chloride added as solid potassium chloride; values of b are not subject to a simple interpretation since the ionic strength varies somewhat during the run. [h] Iron(II) and iron(III) present in titrating solution; both ionic strength and hydrogen ion concentration remain constant during a titration. [i] $C_{III} = 2.1 \times 10^{-3}\ M;$ $C_{II} = 1.7 \times 10^{-3}\ M.$ [j] The average deviations given pertain to a comparison of observed electromotive force and the value calculated using equation 3 with the tabulated values of a and b.

data obtained by Olerup[4] at 20° and $I = 2\ M$ fit equation 4 with values of r which depend upon wave length: $\lambda = 227\ m\mu,\ r = 2.5_4;\ \lambda = 303\ m\mu,\ r = 2.5_7;\ \lambda = 333\ m\mu,\ r = 3.1_2;$ and $\lambda = 384\ m\mu,\ r = 1.8_1.$

At 25°, ~0.16% of uncomplexed iron(III) is present as hydroxyiron(III) ion and ~10^{-5}% is present as $Fe_2(OH)_2^{+4}$. The latter species certainly does not contribute to the light absorption. Although the contribution from hydroxyiron(III) ion to light absorption may be appreciable and, therefore, influence the value of a_0, its effect upon r will be smaller than the experimental uncertainty in this quantity.

Calorimetric Measurements.—In its essential features, the calorimeter was that constructed by Dr. K. Schug, described in earlier papers.[8b,12] The present study was carried out at the time of the study of the mercury(II)-

chloride system,[12] and calibration runs already reported are relevant in the present work.

One type of experiment consisted of breaking a bulb containing iron(III) perchlorate and perchloric acid in the Dewar flask of the calorimeter containing perchloric acid and hydrochloric acid. A series of such experiments was performed at $I = 1.0\ M$ using the three stock solutions of iron(III) perchlorate; a series using stock solution C was performed at $I = 3.7\ M$. The exothermic dilution of each stock solution into perchloric acid solution giving a solution of $I = 1.0\ M$ was studied independently; values of the heat of dilution were found to be −5.6 ± 0.1, −2.4$_2$ ± 0.1, and −0.54 ± 0.01 kcal./mole of iron(III) for stock solutions A, B and C, respectively; in adding solution C to perchloric acid to give a solution of $I = 3.7\ M$, the heat of dilution was −0.24 ± 0.01 kcal./mole of

Table II

Values of r and s (Equation 4) which Correlate Absorbancy Data on Iron(III)–Chloride Solutions[a]

$C_{III} = 1.48 \times 10^{-4}\ M$, $[H^+] = 1.00\ M$, $\{[Cl^-] + [ClO_4^-]\} = 1.00\ M$.

λ (mμ)	—25.0°—		—35.0°—		—45.0°—	
	r	$s \times 10^{-3}$	r	$s \times 10^{-3}$	r	$s \times 10^{-3}$
400	1.01 ± 0.32	0.42	1.32_6	0.44	1.68	0.50
380	1.86 ± 0.34	0.85	2.30	0.92	2.76	1.01
360	2.55	1.68	3.12	1.77	3.88	1.84
335	2.95 ± 0.09	2.42	3.64 ± 0.16	2.46	4.52 ± 0.16	2.50
320	2.86	2.08	3.55	2.10	4.22	2.16
300	2.27 ± 0.06	1.33	2.92	1.33	3.19	1.42
230	2.82	6.18	2.93	6.11	3.82	6.49
220	3.16 ± 0.22	6.85	3.49	6.73	4.31	7.11
Av. diff. in log I_0/I {Calcd. (eq. 4) − obsd.}	0.002		0.004		0.0003_6	

[a] Values of r given with an uncertainty, which is that corresponding to the 95% confidence level, were calculated using a least square procedure for the I.B.M. 704 Computer through the courtesy of Dr. A. J. Zielen of the Argonne National Laboratory.

iron(III). The heat effect observed when iron(III) perchlorate solution was added to solutions containing hydrochloric acid was corrected for the heat of dilution into perchloric acid, it being assumed provisionally that the heat of dilution of a particular stock solution of iron(III) perchlorate is a function only of the ionic strength of the resulting solution and not of the identity of the principal anion present, perchlorate ion or chloride ion. In no stock solutions was the amount of iron(III) present as aquoiron(III) ion calculated to be less than 99% of the stoichiometric concentration. In Table III are presented corrected values of q, the heat absorbed per mole of iron-(III), a function of the stoichiometric concentration of chloride ion.

Two series of experiments were performed in which a small volume of hydrochloric acid in the bulb was broken into a solution of iron(III) perchlorate in perchloric acid. Correction for the heat of dilution was determined by adding hydrochloric acid to perchloric acid to give a solution of $I = 1.0\ M$. Results of these experiments are presented in Table IV.

Interpretation of Data

Data presented relevant to evaluation of the equilibrium quotient for reaction 1 are: (a) electromotive force data which at a given temperature and ionic strength are correlated by equation 3, and (b) spectrophotometric data at $I = 1.0\ M$ which at a given temperature are correlated by equation 4. In a simple interpretation, a of equation 3 and r of equation 4 are identified as Q_1, the equilibrium quotient for reaction 1. How are these quantities to be interpreted if activity coefficients depend upon the composition of solutions of constant ionic strength according to equation 1?

Electromotive Force Data.—For solutions used in the electromotive force measurements, applica-

Table III

The Net Heat Absorbed per Mole of Iron(III) when Iron(III) is Added to Hydrochloric Acid–Perchloric Acid Solution

$I = 1.0\ M$		$T = 25°$	
Soln. A		Soln. C	
$C_{III} = 0.0026$–$0.052\ M$		$C_{III} = 0.006$–$0.013\ M$	
$[Cl^-]$	$q_{corr.}$[a]	$[Cl^-]$	$q_{corr.}$[a]
0.119	0.94	0.113	1.01
.132	1.05	.227	1.79
.229	1.61	.341	2.38
.352	2.04	.450	2.82
.477	2.62	.569	3.14
.538	2.80	.685	3.37
.635	3.02	.787	3.66
.760	3.40	.910	3.86
.804	3.46	.965	4.10
.846	3.58		
.941	3.71	$I = 3.7\ M$	
		0.224	2.46
Soln. B		.450	2.98
$C_{III} = 0.012$–$0.015\ M$		.674	3.17
0.106	1.07[b]	.904	3.34
.212	1.84[c]		
.318	2.36[b]		
.425	2.82[c]		
.530	3.19		
.637	3.52[b]		
.739	3.80		
.846	4.04[b]		

[a] Corrected for heat of dilution as described in text. The dimensions of $q_{corr.}$ are kcal./mole iron(III). [b] The average of two experiments. [c] The average of three experiments.

tion of equation 1 gives

$$\log Q_1 = \log K_1 + (\text{function of } I) +$$
$$[Cl^-]\{b_{72} - b_{32} + b_{34} - b_{74}\} +$$
$$C_{III}\{b_{34} + 3b_{72} - 3b_{32} - 6b_{14}\} +$$
$$C_{II}\{b_{64} + b_{72} - b_{32} - 3b_{14}\} \quad (5)$$

$I = 1.0\ M$		$T = 25°$	
5.17 M HCl in bulb		5.77 M HCl in bulb	
$C_{III} = 0.02$–$0.04\ M$		$C_{III} = 0.009$–$0.011\ M$	
[Cl⁻]	$q_{corr.}{}^{a}$	[Cl⁻]	$q_{corr.}{}^{a}$
0.114	0.89	0.129	1.09[b]
.117	0.90	0.161	1.4[b]
.161	1.29		
.169	1.29		

[a] Corrected for heat of dilution as described in text. The dimensions of $q_{corr.}$ are kcal./mole iron(III). [b] The average of two experiments.

if one neglects the term $[FeCl^{+2}]\ (b_{74} + b_{72} - b_{32} - 3b_{14})$ and assumes $[Fe^{+3}] = C_{III}$. In deriving this equation, the concentrations of perchlorate ion and hydrogen ion were eliminated by using equations for the ionic strength and electroneutrality condition. (An equation of great complexity results from taking into account that iron(III) was present both as aquoiron(III) ion and as monochloroiron(III) ion in relative amounts depending upon the chloride ion concentration.) For concentrations of iron(II) and iron(III) low enough to make the last two terms negligible, equation 5 has the form

$$\log Q_1 = \log K_1 + (\text{function of } I) + B_1[Cl^-] = \log Q_1° + B_1[Cl^-] \quad (5a)$$

in which B_1 is the combination of interaction coefficients $\{b_{72} - b_{32} + b_{34} - b_{74}\}$, and $Q_1°$ is the equilibrium quotient valid for a perchloric acid solution of the ionic strength under consideration in which the reactant species are present at negligibly low concentrations. Substitution of this relationship into the equation for $F_0([Cl^-])$ gives

$$F_0([Cl^-]) = 1 + Q_1°[Cl^-] + (Q_2° + 2.3Q_1°B_1)[Cl^-]^2 + \ldots \quad (6)$$

in which $Q_2°$ is the equilibrium quotient $[FeCl_2{}^+]/[Fe^{+3}][Cl^-]^2$ appropriate for a perchloric acid solution of the ionic strength in question.

Equation 2 giving $E = f([Cl^-])$ contains two additional terms. One is the logarithm of an activity coefficient ratio, which can be expressed

$$\log \left\{ \frac{f_3 \cdot f_{5Cl}}{f_{3Cl} \cdot f_5} \right\} = [Cl^-]\{b_{54} - b_{52} + b_{32} - b_{34}\} \quad (7)$$

this can be simplified to

$$\frac{f_3 \cdot f_{5Cl}}{f_{3Cl} \cdot f_5} \cong 1 + 2.3B'[Cl^-] + \ldots \quad (7a)$$

in which $B' = \{b_{54} - b_{52} + b_{32} - b_{34}\}$, if

$B'[Cl^-] \ll 1$. Calculation of this activity coefficient ratio using equation 7a is not possible since b_{34} is not subject to direct measurement. The other is E_L, dependence of which upon composition of the solution in the chloride-containing half-cell probably is

$$E_L \cong \beta[Cl^-] \quad (8)^{20}$$

Equation 8 does not, however, solve the liquid junction potential problem, for the value of β is inaccessible.

Substitution of equations 6, 7a, and 8 into equation 2 gives

$$\frac{(10^{FE/2.3RT} - 1)}{[Cl^-]} = \left\{ Q_1° + 2.3B' + \frac{F\beta}{RT} \right\} +$$
$$[Cl^-] \left\{ Q_2° + 2.3B_1Q_1° + \frac{(2.3B')^2}{2} + \right.$$
$$2.3B'Q_1° + \frac{F\beta Q_1°}{RT} + \frac{2.3B'F\beta}{RT} + \left. \left(\frac{F\beta}{RT} \right)^2 \right\} +$$
$$[Cl^-]^2 \ \{\ldots\ldots\} \ + \ \ldots \quad (9)$$

Although empirical correlation of the electromotive force data with equation 3 is consistent with equation 9, the intercept a cannot be rigorously identified as $Q_1°$. In identifying the intercept as $Q_1°$, a particular relationship between the experimentally inaccessible quantities B' and β, $B' = -F\beta/2.3RT$, is selected. Different values for $Q_1°$ would be obtained at each temperature and ionic strength if B' and $-(F\beta/2.3RT)$ were assumed to differ by some particular arbitrarily selected amount. The problem of relating the values of β and B' contains the problem of defining a borderline between associated monochloroiron-(III) ion and unassociated iron(III) and chloride ion.[21]

In the simplest interpretation of equation 3, b would be interpreted as Q_2. In the more exact interpretation being considered here, the significance of b is complicated, and its values tabulated in Table I will not be interpreted; they serve to summarize the experimental observations.

The data presented in Table I suggest a mild dependence of a (equation 3) upon C_{II} and C_{III}. This can arise from the terms involving C_{II} and C_{III} in equation 5.[22] The dependence is such that iron concentrations $\{C_{II} + C_{III}\} < 10^{-2}$

(20) G. Biedermann and L. G. Sillen, *Arkiv Kemi*, **5**, 425 (1953).
(21) (a) P. G. M. Brown and J. E. Prue, *Proc. Roy. Soc.* (London), **A, 232**, 320 (1955); (b) W. G. Davies, R. J. Otter, and J. E. Prue, *Discussions Faraday Soc.*, **24**, 103 (1957); (c) G. N. Lewis and M. Randall (revised by K. S. Pitzer and L. Brewer), "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1961, pp. 587–591.
(22) Such a dependence of electromotive force upon the total iron concentration led Olerup (ref. 4) to suggest association of iron(II) ion and chloride ion.
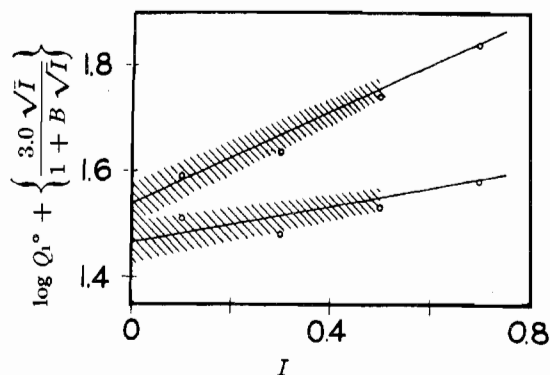
Fig. 2.—The evaluation of $K_1°$ at 25°. Plots of log $Q_1° + \{3.0\sqrt{I}/(1 + B\sqrt{I})\}$ vs. I. Upper line $B = 1.0$. Lower line $B = 1.5$. The shaded region defines an uncertainty of $\pm 5\%$ in $Q_1°$ at $I = 0.5M$ and $\pm 10\%$ at $I = 0$. The intersections of the straight lines and the axis correspond to $K_1° = 35$ and 29.

M exert a negligible effect upon a.

Although uncertainty cloaks the identification of a as $Q_1°$, it seems worthwhile, nevertheless, to extrapolate values of $Q_1°$ to zero ionic strength. This is done in Figure 2, which demonstrates the difficulty in extrapolating equilibrium quotient values of moderate quality obtained at $I \geq 0.1$ M to a unique value corresponding to $I = 0$. This uncertainty is only part of the story for by adoption of other conventions in treatment of the data, different values for $Q_1°$ would have been obtained. The discussion of others regarding extrapolating data pertaining to association of hydroxide ion and calcium ion[23] or hydrogen ion and sulfate ion[24] is an adequate preparation for expecting ambiguity in values of the equilibrium constant for association of aquoiron(III) ion and chloride ion.

Values of a identified as $Q_1°$ from the experiments at $I = 1.0$ M over the range of temperature 14.3–44.3° were used to derive values of $\Delta H_1°$ and $\Delta S_1°$ of $+4.4$ kcal. mole^{-1} and $+16.9$ cal. mole^{-1} deg.$^{-1}$, respectively. Values of $Q_1°$ calculated using these parameters are 2.22 (14.3°), 2.33 (16.3°), 2.92 (25.0°), 3.31 (30.1°), 3.74 (35.4°), and 4.57 (44.3°); these can be compared with experimental a values given in Table I. (Although a better fit can be achieved by allowing a non-zero value for $\Delta C_p°$, the precision of the $Q_1°$ values probably does not warrant use of this additional parameter in interpretation of these data.)

(23) R. G. Bates, V. E. Bower, R. G. Canham, and J. E. Prue, *Trans. Faraday Soc.*, **55**, 2062 (1959).

(24) W. Hamer, "The Structure of Electrolytic Solutions," John Wiley and Sons, New York, N. Y., 1959, p. 236.

Spectrophotometric Data.—Identification of r as $Q_1°$ (equation 4) cannot be valid for all wave lengths since different values were obtained at different wave lengths. The situation resembles that existing in the plutonium(VI)-chloride system treated by Newton and Baker,[19b] who concluded that dependence of r upon wave length indicates: (1) complexes other than one to one species are present at appreciable concentrations, (2) Q_1 varies with the concentration of chloride ion, or (3) the absorbancy index of the complex varies with the concentration of chloride ion. That one or both of the last two conditions applies in the iron(III)–chloride system is indicated by dependence of the ratio $(\tilde{a} - a_0)_{335}/(\tilde{a} - a_0)_{380}$ upon chloride ion concentration.[19b] At 25, 35, and 45°, values of this ratio vary by ~17% in going from 0.20 to 0.95 M chloride ion.

Connick and Coppel[2] reported values of the absorbancy index for monochloroiron(III) ion at 350–390 mμ obtained by using $Q_1 = 4.03$ at $I = 1.0$ M.[7] Values of the product of 4.03 and these values of absorbancy index agree with our values of $r \times s$ obtained at 25° within an average difference of ~4%, indicating consistency between experimentally measured quantities in the two studies.

Values of r obtained at 25° from data at wave lengths of maximum absorption are essentially equal, $r = 2.95 \pm 0.09$ at 335 mμ and $r = 3.16 \pm 0.22$ at 220 mμ. The more reliable of these values agrees closely with the value of a obtained from electromotive force measurements ($a = 2.89$). It is appealing, therefore, to suggest absence of medium effects upon a_1 at this wave length of an absorption peak and to accept this value of r as the value of Q_1 determined by spectrophotometric means. If the possible presence of dichloroiron(III) ion and medium effects upon Q_1 are neglected, the dependence of r upon wave length must be due to a medium effect upon the absorbancy index of monochloroiron(III) ion at wave lengths distant from 335 mμ. Values of $(s - a_0)$ calculated using

$$(s - a_0) = (a - a_0)\{1 + 1/(2.95[\text{Cl}^-])\}$$

and absorbancy data obtained at 300 mμ and 380 mμ are

[Cl$^-$]	0.20	0.40	0.60	0.80	0.95
$10^{-3}(s - a_0)_{300}$	0.99$_4$	1.04	1.06	1.08	1.09
$10^{-3}(s - a_0)_{380}$	0.62$_4$	0.66$_7$	0.68	0.71$_3$	0.73$_5$

In interpretation of equation 4 in terms of one to one association, s is identified as a_1, the absorbancy

index of monochloroiron(III) ion. Whether these calculated variations in a_1 of $\sim 10\%$ and $\sim 18\%$ are reasonable medium effects cannot be settled with any certainty.[25] Admittedly there is a fine line of distinction between allowing for a medium effect upon a_1 due to chloride ion replacing perchlorate ion and allowing for formation of dichloroiron(III) ion. Before accepting this interpretation of the spectrophotometric data, consideration will be given to an interpretation involving formation of appreciable dichloroiron-(III) ion.

As shown by Kruh[26] and Baes,[27] and discussed at length by Newton and Baker,[19b] conformity of spectral data to equation 4 does not rule out appreciable dichloroiron(III) ion in the chloride concentration range studied. Strict adherence to the relationships derived by Kruh would, for a system involving Fe^{+3}, $FeCl^{+2}$, and $FeCl_2^+$ with medium-independent values of Q_1 and $\{a_i - a_0\}$ ($i = 1$ and 2), lead to but *two* different values of r, the apparent value of Q_1, one value associated with each of two allowed values of $(a_2 - a_0)/(a_1 - a_0)$

$$\frac{a_2 - a_0}{a_1 - a_0} = \frac{1 \pm \sqrt{1 - 4Q_2/Q_1^2}}{2Q_2/Q_1^2}$$

More than two different values of r correlate the data of this study. Considering the experimental uncertainty, it is probable, however, that all of the data are consistent with particular pairs of values of Q_1 and Q_2. Using the procedure of Newton and Baker, it can be shown, for instance, that sets of values $\{Q_1 = 4.35, Q_2 = 4.0\}$ or $\{Q_1 = 4.75, Q_2 = 5.0\}$ coupled with appropriate values of a_1 and a_2 correlate the data at wave lengths 400 mμ, 335 mμ, and 200 mμ.

If one also allows for a dependence of Q_1 upon chloride ion concentration (equation 5a) and a linear dependence of a_1 upon chloride ion concentration in solutions of constant ionic strength

$$a_1 = a_1^0 + d_1[Cl^-] \qquad (10)$$

one obtains an equation for $(\tilde{a} - a_0) = f([Cl^-])$ similar in form to that considered by Kruh[26] and Baes.[27] The coefficient of $[Cl^-]$ in the numerator is $(a_1^0 - a_0)Q_1^0$ and in the denominator is Q_1^0; the coefficients of $[Cl^-]^2$ in the numerator and denominator contain contributions from medium effects upon Q_1 and a_1 as well as quantities

pertaining to the second complex. If one neglects in both numerator and denominator all terms with the concentration of chloride raised to the third (or higher) power, the mathematical problem is the same as that treated by Kruh[26] and Baes.[27] This interpretation of the dependence of r upon wave length identifies the values of Q_1 given in the previous paragraph as values of Q_1^0; these values do not agree with the value obtained in the electromotive force studies. A further objection to accepting the value of Q_1^0 obtained in this treatment is its consequences in interpretation of the calorimetric data, to be discussed.

We accept, therefore, the identification of r obtained from measurements at 335 mμ as Q_1^0. Values of r obtained at 220 mμ, another wave length of maximum absorption, agree with values obtained at 335 mμ. The values of Q_1^0 so obtained at 25, 35, and 45° at 335 mμ yield values of ΔH_1^0 and ΔS_1^0 equalling 4.0_5 kcal. mole^{-1} and 15.7 cal. mole^{-1} deg.$^{-1}$, respectively. Consequences of this interpretation are both a negligible medium effect upon Q_1 as the relative concentrations of chloride ion and perchlorate ion vary at constant ionic strength and negligible formation of dichloroiron(III) ion in the solutions studied. The dependence of r upon wave length shown in Table II then must be caused by an appreciable dependence of the absorbancy index of monochloroiron-(III) ion upon the relative concentration of chloride ion and perchlorate ion, a dependence having the fortuitous consequence of allowing equation 4 to correlate the data within experimental error.

The value of ΔH_1^0 obtained in this spectrophotometric study is in substantial agreement with values obtained in our electromotive force and calorimetric studies and also with values obtained in spectrophotometric studies by Sutin, Rowley, and Dodson[28] and Coll, Nauman, and West,[29] in both of which the wave length of maximum absorption was studied. It does not agree with values obtained in spectrophotometric studies by Rabinowitch and Stockmayer[7] and Connick and Coppel,[2] in both of which the wave lengths under consideration did not correspond to absorption maxima.

The present work demonstrates the danger of studying light absorption at a single wave length,

(25) (a) M. C. R. Symons, *Discussions Faraday Soc.*, **24**, 117 (1957); (b) D. A. L. Hope, R. J. Otter, and J. E. Prue, *J. Chem. Soc.*, 5226 (1960).

(26) R. F. Kruh, *J. Am. Chem. Soc.*, **76**, 4865 (1954).

(27) C. F. Baes, *J. Phys. Chem.*, **60**, 878 (1956).

(28) N. Sutin, J. K. Rowley, R. W. Dodson, *ibid.*, **65**, 1248 (1961).

(29) H. Coll, R. V. Nauman, and P. W. West, *J. Am. Chem. Soc.*, **81**, 1284 (1959).

particularly one distant from an absorption peak.[25a] If only 380 mμ had been studied, the calculated values of Q_1 would be ~1.6-fold lower at each temperature than the values which we consider correct, those calculated from data at 335 mμ. The value of ΔH_1 calculated from such data would, therefore, be essentially equal to the correct value. The value of ΔH_1, calculated from the temperature dependence of $\{r \times s\}$ (equation 4), which is equal to the temperature dependence of the absorbancy of a solution of a particular composition with [Cl$^-$] $\ll Q_1$, would not, however, be essentially correct. Values of $\{-R$ d ln $(r \times s)/d(1/T)\}$ obtained using our data range from 3.8 kcal./mole (300 mμ) to 5.9 kcal./ mole (400 mμ).

Calorimetric Data.—Our concern with medium effects in solutions of constant ionic strength but varying concentration of chloride ion extends to the heat of dilution of acidic iron(III) perchlorate solution. Corrected values of the heat absorbed when iron(III) perchlorate was added to solutions containing chloride ion, $q_{corr.}$, reported in Table III were obtained by assuming the absence of such a medium effect. If, in addition to the dependence of Q_1 upon the concentration of chloride ion given by equation 5b, the chloride ion concentration dependences of ΔH_1 and $q_{dil.}$ are assumed to be

$$\Delta H_1 = \Delta H_1{}^\circ + h[\text{Cl}^-] \tag{11}$$

$$q_{dil.} = q^\circ{}_{dil.} + c[\text{Cl}^-] \tag{12}$$

the dependence of $q_{corr.}$ upon [Cl$^-$] is given by

$$\frac{q_{corr.}\,(1 + Q_1{}^\circ[\text{Cl}^-])}{Q_1{}^\circ[\text{Cl}^-]} = \left\{\Delta H_1{}^\circ + \frac{c}{Q_1{}^\circ}\right\} +$$
$$[\text{Cl}^-]\left\{h + c + \frac{\Delta H_2{}^\circ}{Q_1{}^\circ} + B\Delta H_1{}^\circ\right\} +$$
$$[\text{Cl}^-]^2\,\{....\} + ... \tag{13}$$

Data obtained using iron(III) perchlorate stock solution C are plotted in Figure 3. The value of $Q_1{}^\circ$ obtained as a in our electromotive force studies at 25° was used in interpretation of the calorimetric data. It is unfortunate that $c/Q_1{}^\circ$ cannot be separated from $\Delta H_1{}^\circ$ in equation 13, and there is, therefore, an uncertainty in interpreting the intercept in Figure 3 as $\Delta H_1{}^\circ$. For experiments using stock solution C, the uncertainty should be smaller than that in experiments using more concentrated stock solutions (A and B). The value of $\Delta H_1{}^\circ$ for a medium of 1.0 M perchloric acid, obtained as the intercept in Figure 3, is 4.2 kcal./mole. Experiments using iron(III) solutions A and B
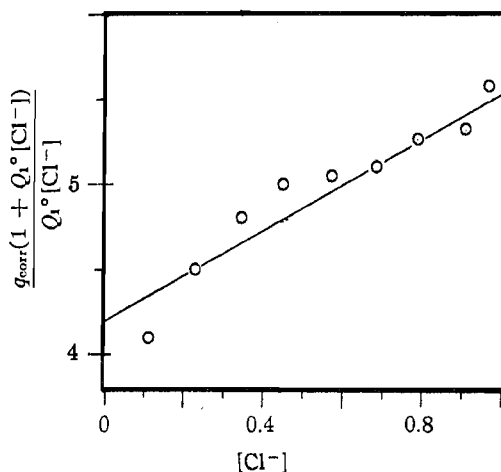

Fig. 3.—The evaluation of $\Delta H_1{}^\circ$ at 25°. Plot of $q_{corr.}$ $(1 + Q_1{}^\circ[\text{Cl}^-])/Q_1{}^\circ$ [Cl$^-$] *vs.* [Cl$^-$]. The intercept is $\{\Delta H_1{}^\circ + c/Q_1{}^\circ\} = \Delta H_1{}^\circ$.

yield similar plots with intercepts 3.9 and 4.6 kcal. mole^{-1}, respectively. Values of the slopes of linear plots for the three series are 1.4$_3$, 1.3$_3$, and 1.3$_2$ kcal. mole^{-2} l. The four experiments at $I = 3.7\ M$ yield values of $q_{corr.}$ which are correlated by the equation

$$q_{corr.}\,(1 + Q_1{}^\circ[\text{Cl}^-])/(Q_1{}^\circ[\text{Cl}^-]) = 3.4_3 + 0.28[\text{Cl}^-]$$

In view of the complicated nature of the coefficient of [Cl$^-$] on the right hand side of equation 13, no interpretation of the slope in plots such as Figure 3 will be attempted, although attention is called to its smaller magnitude at $I = 3.7\ M$.

Values of ΔH_1 at $I = 1.0\ M$ obtained from data presented in Table IV range from 3.6 to 4.4 kcal./ mole. In calculation of these values, a value of $Q_1 = 2.88$ was used.

One possible interpretation of the spectrophotometric data led to values of $Q_1{}^\circ$ as high as 4.75 Use of this value in a plot such as Figure 3 leads to an intercept of ~2.2 kcal./mole, which is quite inconsistent with the value of ΔH_1 obtained from electromotive force studies.

Discussion

Although taking possible medium effects in solutions of constant ionic strength into account contributes uncertainty to the interpretation of each kind of data obtained in the present study, provisional values of $Q_1{}^\circ$ and $\Delta H_1{}^\circ$ obtained in the independent studies are essentially equal. On the basis of the present work, we select, therefore, the following values for the thermodynamic quantities of interest

Medium	Q_1° (25°)	ΔH_1° ($\times$ mole kcal.$^{-1}$)	ΔS_1° ($\times$ mole deg. cal.$^{-1}$)
1.0 M HClO$_4$	2.9 ± 0.1	4.3 ± 0.3	16.7 ± 1
3.7 M HClO$_4$	10.7 ± 1	3.4 ± 0.3	16.1 ± 1

The value of ΔS_1° for 3.7 M perchloric acid can be compared directly with the value $\Delta S_1^{\circ} = 17.2$ cal. mole^{-1} deg.$^{-1}$ for the reaction

$$Cr(OH_2)_6{}^{+3} + Cl^- = Cr(OH_2)_5Cl^{+2} + H_2O$$
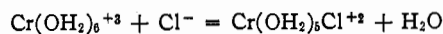
in the same medium.[8] The similarity of these values suggests very strongly that the iron(III) reaction, like the chromium(III) reaction, involves no change in the coördination number of the metal ion.

To what extent does close agreement of values of ΔS_1° for the iron(III) and chromium(III) reactions indicate that the conventions adopted in treating the electromotive force data have resulted in defining the monochloroiron(III) ion produced in reaction 1 as the inner-sphere complex Fe-$(OH_2)_5Cl^{+2}$? If there is such an entity as a well-defined outer-sphere complex, which does not seem at all certain, ΔS° for the reaction

$$Fe(OH_2)_6{}^{+3} + Cl^- = Fe(OH_2)_6{}^{+3} \cdot Cl^-$$
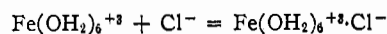
would be expected to be less positive than ΔS° for the reaction forming the inner-sphere complex. The value of ΔS° for formation of one mole of monochloroiron(III) ion, x moles of which is outer-sphere species and $(1 - x)$ moles of which is inner-sphere species is

$$\Delta S_1^{\circ} = x\Delta S_{1,o}{}^{\circ} + (1 - x)\Delta S_{1,i}{}^{\circ} -$$
$$R(x \ln x + (1 - x) \ln (1 - x))$$

in which $\Delta S_{1,o}$ and $\Delta S_{1,i}$ are values of the entropy change for reactions forming outer-sphere and inner-sphere complexes, respectively. Calculated values of $(\Delta S_1^{\circ} - \Delta S_{1,i}{}^{\circ}) \times$ cal.$^{-1}$ deg. mole are

$\{\Delta S^{\circ}_{1,i} - \Delta S^{\circ}_{1,o}\}$ $\times$ deg. cal.$^{-1}$ mole	$x = 0.25$	$x = 0.50$	$x = 0.75$
4	+0.1	−0.6	−1.9
6	−0.4	−1.6	−3.4
8	−0.9	−2.6	−4.9

Because of the entropy of mixing term, inclusion of outer-sphere species in what monochloroiron-(III) ion comprises does not have much effect upon ΔS_1° unless the outer-sphere species is the predominant monochloroiron(III) species. The presence of an appreciable amount of monochloroiron(III) ion as outer-sphere species cannot, therefore, be ruled out on the basis of the similarity of the entropy changes in the iron(III) and chromium(III) reactions.

The Reaction of Titanium Tetrafluoride with Di-*n*-propylamine

BY JOHN A. CHANDLER,[1] JEROME E. WULLER, AND RUSSELL S. DRAGO[2]

The reaction of di-*n*-propylamine with titanium tetrafluoride has been investigated in detail. In all cases studied an aminolysis reaction occurred resulting in $(R_2NH_2^+)_2TiF_6^-$ and R_2NTiF_3. Product isolation, results from conductometric titrations, and an infrared study can be interpreted to eliminate several reaction schemes. A sequence of reactions is proposed which is consistent with the experimental results. A continuous variation study on the system $(R_2NH_2^+)_2TiF_6^-$–TiF$_4$ gives rise to both formulas for the species and conductance data that can be employed to explain the sequence of reactions of TiF$_4$ with the amine.

Introduction

In contrast to the abundance of literature on the reactions of titanium tetrachloride, relatively little is reported on titanium tetrafluoride. Surprisingly, it is reported that titanium tetra-fluoride forms 1:1 addition compounds with methylamine, ethylamine, and aniline.[3] A compound containing two molecules of base to one of TiF$_4$ is reportedly formed with ammonia and both 2:1 and 1:1 addition compounds are reported to form with pyridine.[4] In most of this earlier

(1) Abstracted in part from the Ph.D. Thesis of John A. Chandler, University of Illinois, 1959.
(2) Author to whom correspondence should be addressed.

(3) H. J. Emeleus and G. S. Rao, *J. Chem. Soc.*, 4245 (1958).
(4) O. Ruff and R. Ipsen, *Ber.*, **36**, 1777 (1903).