the charge on the cation or anion undergoing polymerization, and $\bar{n}$ are generally both known, the charge per monomer unit, $Z^{*\prime} = (z + \bar{n} - \bar{\nu})$, can only have values between $z + \bar{n}$ and 0. In order to obtain a system corresponding to the one treated in the hypothetical case, it is necessary to make the measurements at high values of $\bar{n}$. Under these conditions, ψ_2 is considerably greater than ψ_3, and since $\bar{n}$ will have a sign opposite to z the possible values of $Z^{*\prime}$ are limited to a narrow range. In addition, the use of a weakly complexing ionic medium like $NaClO_4$ makes it very unlikely that $\bar{\nu}$ will have values greater than about 0.5. In order to relate the properties of the monomeric component to those of the polymeric component, these quantities are defined

$$Z_2^*/N = Z^{*\prime}, \text{ charge per monomer unit} \quad (17)$$

$$M_2/N = M', \text{ formula wt. of the monomer component} \quad (18)$$

$$m_2 \cdot N = m', \text{ molarity of component 2 computed as monomer} \quad (19)$$

$$\psi' = (dn/dm') \quad (20)$$

Within the relatively narrow range of possible $Z^{*\prime}$ values, values of $Z^{*\prime}$ are assumed and used to calculate c_2, φ_2 and m_3^*. It is convenient to plot the deviation function obtained by substituting (17) and (18) in (12) and rearranging terms

$$\frac{Hc_2M'}{\tau^*} - \frac{10^3Z^{*\prime 2}c_2}{2m^*_3M'} = \frac{1}{N} = \frac{H''\psi'^2m'}{\tau^*} - \frac{Z'^2m'}{2m_3} \quad (21)$$

as a function of c_2 or m'. When the correct value of $Z^{*\prime}$ is chosen, the plot will have a limiting slope of 0 and an intercept $1/N$. This is shown in Fig. 2 in which the turbidity data for the first case in Table I which corresponds to the case with $N = 5$, $M' = 200$, and $Z^{*\prime} = 0.8$ are plotted as deviation functions. Values of M', c_2, m_3^* and φ_2 were computed for $Z^{*\prime} = 0.4$ and 1.2 in addition to the correct value 0.8. In this case, the value chosen for $Z^{*\prime}$ has a significant effect on the value of N; however, the large deviations from 0 slope obtained with incorrect $Z^{*\prime}$ values make a fairly accurate estimate of the charge possible. It should be noted that while deviations from equation 12 limit the accuracy of the determination of $Z^{*\prime}$, the effect of $Z^{*\prime}$ on the intercept decreases rapidly and eventually becomes negligible as the ratio ψ_2/ψ_3 increases. The analysis of highly polydisperse systems is restricted to those where $\psi_2 >> \psi_3$ and $Z^{*\prime}$ is best set equal to 0 in the calculation of N_w.

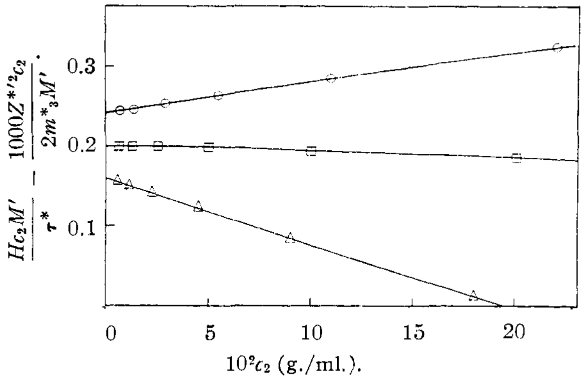

Fig. 2.—Effect of $Z^{*\prime}$ on the determination of N: ○, $Z^{*\prime} = 0.4$; □, $Z^{*\prime} = 0.8$; △, $Z^{*\prime} = 1.2$.

In summary it has been shown that the average degree of polymerization N may be calculated from light scattering measurements on systems at high values of $\bar{n}$. Since N and $Z^{*\prime}$ may also be obtained from sedimentation equilibrium measurements, a system may be studied by two independent experimental methods. Light scattering measurements provide a means of obtaining information about systems at high values of N where data from the more usual e.m.f. and cryoscopic measurements tend to be inconclusive and also provide a convenient method for measuring the aggregation as a function of time in systems where the equilibria are not attained rapidly.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Kinetics of the Formation of the Ferric Chloride Complex

BY ROBERT E. CONNICK AND CLAUDE P. COPPEL

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A previously described apparatus for rapidly mixing two solutions has been used to study the kinetics of the reaction: $Fe^{+++} + Cl^- = FeCl^{++}$ in aqueous solution. The forward rate law has been determined to be $d(FeCl^{++})/dt = k_1(Fe^{+++})(Cl^-) + k_2[(Fe^{+++})(Cl^-)/(H^+)]$. At 25° and an ionic strength of 1.0 M the values of k_1 and k_2 are 9.4 ± 1.0 M^{-1} sec.$^{-1}$ and 18.0 ± 2.0 sec.$^{-1}$, respectively. The heats and entropies of activation were calculated from the variation of the rate with temperature. Mechanisms for the observed rate law are discussed and the rate constants and entropies of activation are compared with those for the analogous thiocyanate reaction. A lower limit for the rate of chloride complexing of iron(III) in 3 M sodium chloride has been obtained from nuclear magnetic resonance studies and compared with the results of the spectrophotometric kinetics studies.

The reaction in aqueous solution of ferric ion with chloride ion to form the monochloride complex $FeCl^{+2}$ is known to be rapid, but apparently no quantitative study of the rate had been made previously. The present work constitutes a determination of the rate law using the fast mixing apparatus which had been applied earlier to the study of the kinetics of the analogous complexing reaction of thiocyanate ion with ferric ion.[1]

Chloride Complexing Constants.—In the interpretation of the data it is necessary to know the equilibrium quotients relating the various species

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[1] J. F. Below, R. E. Connick and C. P. Coppel, THIS JOURNAL **80**, 2961 (1958).

present. The principal equilibria between ferric and chloride ions at low chloride concentration are

$$Fe^{+++} + Cl^- = FeCl^{++} \qquad Q_1 = \frac{(FeCl^{++})}{(Fe^{+++})(Cl^-)} \quad (1)$$

$$FeCl^{++} + Cl^- = FeCl_2^+ \qquad Q_2 = \frac{(FeCl_2^+)}{(FeCl^{++})(Cl^-)} \quad (2)$$

where parentheses indicate concentrations in moles per liter, M. Rabinowitch and Stockmayer[2] in an extensive spectrophotometric study, obtained values of Q_1 and Q_2 at zero ionic strength and 25° of 30 ± 5 and 4.5 ± 2, respectively, and from the ionic strength dependence deduced

$$\log Q_1 = 1.51 - \frac{3\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} + 0.295\mu \quad (3)$$

where μ is the ionic strength. Their temperature dependence results gave a value of ΔH_1 of 8.5 ± 0.2 kcal./mole at an ionic strength of 0.61. Olerup[3] obtained a value of Q_1 of 5.7 at 20° and $\mu = 2.0$, which is to be compared with the value of 5.5 at 25° calculated from equation 3 for an ionic strength of 2. Correction of Olerup's value to 25° using the ΔH_1 value discussed later yields 6.8 for Q_1. Values of Q_1 calculated from equation 3 were used in the present work. Under the conditions employed by Rabinowitch and Stockmayer[2] the polymerization of hydrolyzed ferric ion[4] was negligible, both optically and stoichiometrically.

The work reported here was carried out at an ionic strength (μ) of 1.0 M where the value of Q_1 obtained from equation 3 is 4.03 at 25°. This high ionic strength as compared to 0.40 used in the ferric thiocyanate study[1] was necessary because of the high acidities required to eliminate light absorption of hydrolyzed ferric species in the region of ferric chloride absorption.

It should be noted that there is considerable disagreement in the literature regarding the value of Q_1.[4a] A change in the value of Q_1 would alter the values of k, k_1, k_2 and k_3 approximately in direct proportion to the ratio of the Q_1 values. The primed rate constants in Table III would be essentially unaffected.

The ΔH_1 value (equation 1) of 8.5 ± 0.2 kcal. reported by Rabinowitch and Stockmayer[2] was not used because their data indicate that somewhat more than 20% of the total ferric ion was present as $FeCl^{++}$ and *ca.* 1% as $FeCl_2^{++}$. Under these conditions the method of calculation which we infer from their paper would not yield accurate equilibrium quotients. Since no other value was available, ΔH_1 was remeasured, as described under Experimental; the value found was 6.0 ± 0.1 kcal.

Hydrolysis of Ferric Ion.—All data were corrected for the hydrolysis of ferric ion. Milburn and Vosburgh[4] found the principal equilibria to be

$$Fe^{+++} + H_2O = FeOH^{++} + H^+ \qquad Q_H = \frac{(FeOH^{++})(H^+)}{(Fe^{+++})} \quad (4)$$

$$2FeOH^{++} = Fe_2(OH)_2^{+4} \qquad Q_D = \frac{(Fe_2(OH)_2^{+4})}{(FeOH^{++})^2} \quad (5)$$

with Q_H (25°, $\mu = 1.0$) $= 1.65 \times 10^{-3}$ and Q_D (25°, $\mu = 1.0$) $= 711$. The equilibrium quotients were corrected to other temperatures using ΔH values of 10.2[5,6] and −8.2[6] kcal./mole, respectively, measured for an ionic strength of 1.00.

Interpretation of Rate Data

As a reasonable working hypothesis, it was assumed that the rate law for the ferric chloride complex formation could be written as

$$Fe^{+++} + Cl^- \underset{\bar{k}'}{\overset{\bar{k}}{\rightleftarrows}} FeCl^{++} \quad (6)$$

the integrated rate law being

$$-\bar{k}t = \frac{2.303}{[(Fe^{+++}) + 1/Q_1]} \log \frac{(FeCl^{++})_\infty - (FeCl^{++})}{(FeCl^{++})_\infty - (FeCl^{++})_0} \quad (7)$$

where (Fe^{+++}) is assumed to be constant. Under the experimental conditions used, with a value of Q_1 of about 4 and ferric and chloride ion concentrations of 8×10^{-3} and 4×10^{-3} M, respectively, very little of either the ferric ion or chloride ion is complexed, and therefore the linearity of a log $[(FeCl^{++})_\infty - (FeCl^{++})]$ *versus* time plot does not test directly the dependence of (Fe^{+3}) and (Cl^-). Such linearity does establish, however, a first-order dependence on $(FeCl^{++})$ for the reverse rate. Such plots of the experimental data were in general linear, deviations being present randomly owing to various experimental limitations.

Ferric and Chloride Dependence.—Direct verification of order with respect to ferric and chloride ion concentrations was obtained by varying the initial concentrations of these ions and comparing the $\bar{k}$ values calculated using equation 7. The quantity (Fe^{+3}) in the denominator was almost negligible, *i.e.*, 4% or less of $1/Q_1$, and it was not necessary to know it with any great accuracy, nor to know the mixing ratio accurately. Table I shows the data for runs made at varying ferric and chloride ion concentrations. At a given acidity it is seen that the assumed rate law fits the data within the experimental accuracy but that the rate increases with decreasing acidity. These results in conjunction with the linearity of the log $[(FeCl^{++})_\infty - (FeCl^{++})]$ plots demonstrate the first-order dependence on ferric and chloride ion concentrations over the acidity range investigated. The $\bar{k}$ values at 25° in the last column of Table I were calculated from those in column 5 using the ΔH^* values which will be discussed under Temperature Dependence.

Acid Dependence.—Figure 1 shows a plot of $\bar{k}$ at 25° *versus* $1/(H^+)$. Except for the points at lowest hydrogen ion concentration, the plot is linear with a finite intercept at $1/(H^+) = 0$ and can be interpreted as representing the rate law

$$\frac{d(FeCl^{++})}{dt} = k_1(Fe^{+++})(Cl^-) + k_2\frac{(Fe^{+++})(Cl^-)}{(H^+)}$$

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(2) E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(3) H. Olerup, *Svensk. Kem. Tidskr.*, **55**, 324 (1943).

(4) R. M. Milburn and W. C. Vosburgh, THIS JOURNAL, **77**, 1352 (1955).

(4a) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1957; H. Coll, R. V. Nauman and P. W. West, *ibid.*, **81**, 1284 (1959).

(5) T. H. Siddall and W. C. Vosburgh, THIS JOURNAL, **73**, 4270 (1951).

(6) R. M. Milburn, *ibid.*, **79**, 537 (1957).

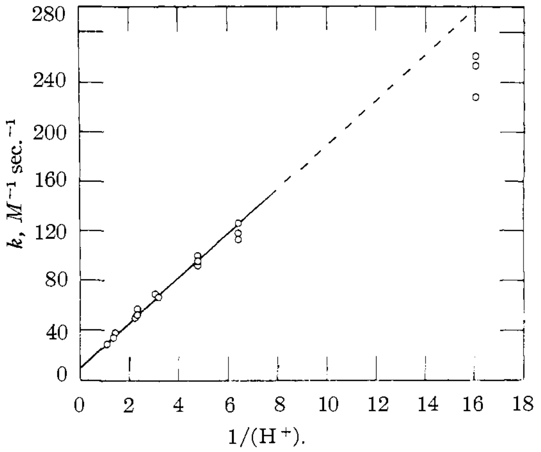

Fig. 1.—The acid dependence of $\bar{k}$ at 25° and μ = 1.0 (NaClO$_4$ added).

where $\bar{k} = k_1 + k_2/(\mathrm{H}^+)$ and the back reactions have been omitted for simplicity. The values of $\bar{k}$ at $(\mathrm{H}^+) = 0.90$ and 0.311, which were taken from the temperature dependence data (see later), were given more weight because they represent entire series of runs.

TABLE I

KINETIC DATA ON FERRIC AND CHLORIDE DEPENDENCE (FOR μ = 1.0, NaClO$_4$ ADDED)

Temp. (°C.)	ΣFe(III) (M × 10^3)	ΣCl$^-$ (M × 10^3)	(H$^+$) (M)	$\bar{k}$ (M^{-1} sec.$^{-1}$)	$\bar{k}$ (25°) (M^{-1} sec.$^{-1}$)
24.11	9.8	4.3	0.89	26.8	29.9
23.7	9.5	4.3	.89	25.0	29.4
23.41	5.0	4.0	.90	22.6	27.4
22.06	2.0	18.5	.90	20.0	28.7
22.96	5.6	5.3	.90	20.1	26.2
22.41	8.5	4.7	.156	88.5	125.8
23.68	8.2	4.6	.156	95.0	113.2
25.75	1.7	4.5	.156	130.1	118.0
24.80	1.7	4.5	.156	109.1	112.0
22.8	3.1	15.9	.0622	183	261
27.9	8.1	4.7	.0622	259	227
26.6	3.4	15.4	.0622	228	253

At the lowest hydrogen ion concentration studied (0.0622 M) significant deviations from the linear relationship appear. These are believed to be due to mixing limitations which become important at these low acidities, *i.e.*, the slowness of mixing becomes partially rate determining. At this acidity and at sweep frequencies of 60 c.p.s. the reaction could only be observed for approximately two sweeps; the mixing process itself took about 1 sweep (16 mseconds) for 83% mixing.

The intercept and slope of Fig. 1 give values of k_1 = 9.4 ± 1.0 M^{-1} sec.$^{-1}$ and k_2 = 18.0 ± 2.0 sec.$^{-1}$.

Temperature Dependence.—Experiments were run covering the temperature range 16 to 32°; the results are shown in Table II. Because of the hydrogen ion dependence of $\bar{k}$ the runs were made at two acidities. From the data in Table II and the first five experiments of Table I, a plot was made of log $\bar{k}/T$°K. *versus* 1/T°K. for the two acidities. Since the data showed no significant signs of curvature, the best fitting straight lines were drawn. The average deviation from these lines was less than 5%. Values of $\bar{k}$ were taken from this plot at three temperatures corresponding to 1000/T°K. = 3.28, 3.36 and 3.44, and from these were calculated values of k_1 and k_2 at these three temperatures. Figure 2 shows a plot of log k_1/T°K. *versus* 1000/T°K. and similarly for k_2. From the slopes of these lines, ΔH_1^* = 16.6 ± 2.0 kcal./mole and ΔH_2^* = 23.3 ± 2.0 kcal./mole were calculated.

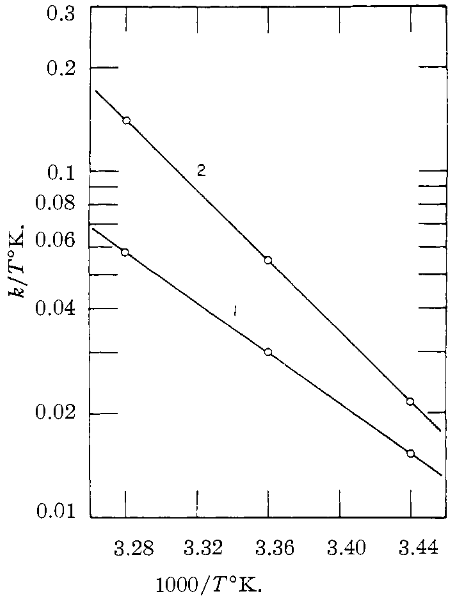

Fig. 2.—The temperature dependence of k_1 (curve 1) and k_2 (curve 2).

TABLE II

TEMPERATURE DEPENDENCE RESULTS (AT μ = 1.0, NaClO$_4$ ADDED)

Temp. (°C.)	ΣFe(III)[a] (M × 10^3)	(ΣCl$^-$)[a] (M × 10^3)	(H$^+$) (M)	$\bar{k}$ (M^{-1} sec.$^{-1}$)
31.29	6.3	4.9	0.90	59.3
31.74	6.6	4.7	.90	66.5
23.95	6.9	4.6	.90	24.8
18.16	6.4	4.8	.90	12.2
15.97	8.0	4.7	.90	9.45
31.72	7.8	4.8	.90	69.1
25.03	8.0	4.8	.90	30.4
22.23	8.0	4.7	.90	20.0
31.45	7.9	4.7	.311	154.7
16.97	7.6	4.8	.311	23.0
24.00	7.8	4.7	.311	62.9
18.40	7.6	4.8	.311	28.2
21.23	7.7	4.8	.311	40.5
26.24	7.5	4.9	.311	74.3
32.28	7.4	4.9	.311	161.2

[a] Total stoichiometric concentration.

The corresponding entropies of activation at 25° are ΔS_1^* = 2 ± 6 e.u. and ΔS_2^* = 25 ± 6 e.u. The values of k_1 = 9.4 M^{-1} sec.$^{-1}$ and k_2 = 17.5 sec.$^{-1}$ from this plot are in good agreement with the values 9.4 and 18.0 obtained from the hydrogen ion dependence results. The uncertainties were obtained by assuming a possible error of 10% in k_1 and k_2 at the high and low temperatures.

Recently King and Gallagher[7] have made calorimetric measurements on the heat of reaction 1, ΔH_1, and found a provisional value of *ca.* 4.3 ± 0.4 kcal. rather than 6.0 kcal. measured here. Use of their value would lower ΔH_1^* and ΔH_2^* approximately 1.7 kcal. and lower ΔS_1^* and ΔS_2^* approximately 6 e.u. The source of the discrepancy in the ΔH_1 values is not certain. Our spectrophotometric value could be in error through failure of the assumption that the molar absorptivity of $FeCl^{+2}$ is independent of temperature[8]; the calorimetric value is relatively sensitive to errors in the equilibrium quotient of reaction 1 at 25°.

Discussion of the Rate Law

Mechanisms analogous to those of the thiocyanate reaction[1] can be proposed for the two terms of the ferric chloride rate law

$$Fe(H_2O)_6^{+++} + Cl^- \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} Fe(H_2O)_5Cl^{++} + H_2O \quad (a)$$

$$Fe(H_2O)_6^{+++} \overset{Q_H}{\rightleftharpoons} Fe(H_2O)_5OH^{++} + H^+ \quad (b)$$

$$Fe(H_2O)_5OH^{++} + Cl^- \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} Fe(H_2O)_4OHCl^+ + H_2O$$

$$Fe(H_2O)_4OHCl^+ + H^+ \rightleftharpoons Fe(H_2O)_5Cl^{++}$$

where $k_3 = k_2/Q_H$. Mechanisms also could be proposed involving hexa-coördinated activated complexes, where water is released before the complexing ligand enters in the rate-determining step.

The value of k_3 at 25° and $\mu = 1.0$ is 1.1×10^4 M^{-1} sec.$^{-1}$, compared to $k_1 = 9.4$ M^{-1} sec.$^{-1}$. From electrostatics, $FeOH^{++}$ would be expected to react with Cl^- more slowly than does Fe^{+++}, which is opposite to the observed result. This same situation exists in the thiocyanate case and was interpreted[1] as being due to the weakening of the bonding of the hydrated waters by the negative OH^-, thus permitting easier entry of the thiocyanate ion into the coördination sphere, or to some electronic interaction of the OH^- with the Fe^{+3}, resulting in faster reaction with Cl^-. It might be argued that the greater rate of the hydrolyzed species is evidence for a six-coördinated activated complex. The more facile release of electrons from the OH^- group to the ferric ion could help to compensate better for the incomplete bonding of the incoming chloride ion, relative to the corresponding behavior of H_2O. It can be argued equally well, however, that the same effect would operate in the case of the seven-coördinated activated complex, where the incomplete bonding of the incoming and leaving groups would be similarly compensated.

A comparison of the kinetic parameters of the chloride and thiocyanate[1] reactions in Table III is instructive. It is to be noted that the relative values of k_1 follow the stabilities of the complexes rather than the prediction from electrostatics. The more stable and therefore more strongly bonded thiocyanate complex forms more rapidly than the chloride complex. On an electrostatic model, the thiocyanate ion would be expected to be attracted less strongly than chloride ion since the charge in SCN^- is probably spread out through the ion. The weaker hydration of SCN^- would, of course, work in the opposite direction. In contrast to the k_1 values the k_2 values are nearly equal.

TABLE III

COMPARISON OF FERRIC CHLORIDE AND FERRIC THIOCYANATE KINETIC PARAMETERS

	Chloride[a]	Thiocyanate[b]
k_1, M^{-1} sec.$^{-1}$	9.4 ± 1	127 ± 10
k_2, sec.$^{-1}$	18.0 ± 2	20.2 ± 2
k_1', sec.$^{-1}$	2.3 ± 0.2	0.87 ± 0.07
k_2', M sec.$^{-1}$	4.5 ± 0.5	0.138 ± 0.014
$\Delta H_1'^*$, kcal.	10.6 ± 2.0	14.6 ± 1.4
$\Delta H_2'^*$, kcal.	17.3 ± 2.0	21.8 ± 1.4
$\Delta S_1'^*$, e.u.	−21 ± 6	−10 ± 5
$\Delta S_2'^*$, e.u.	2 ± 6	10 ± 5

[a] Ionic strength 1.0 M. [b] Ionic strength 0.40 M.

Until the discrepancy in ΔH_1 for the chloride reaction is resolved (see above), it is useful to consider $\Delta H_1'^*$, $\Delta H_2'^*$, $\Delta S_1'^*$, and $\Delta S_2'^*$, *i.e.*, the quantities for the rate of decomposition of $FeCl^{++}$ and $FeSCN^{++}$, which are nearly independent of the choice of ΔH_1. These values are listed in Table III. The entropies of activation for the chloride complex decomposition reaction are 11 and 8 e.u. more negative than for the corresponding thiocyanate reaction.[9] The difference in ionic strength would not be expected to produce this large a change. The explanation lies perhaps in the greater localization of charge on the Cl^- than on the SCN^- so that the electrostatic effect of separation of charge in the activated complex involving chloride is considerably greater than with thiocyanate. The smallness of the entropies of activation would imply that the solvent is considerably oriented in the activated complex in restricted configurations conducive to the separation of the ions.

Rate of Chloride Complexing from N.m.r. Measurements

Paramagnetic ions in solution cause a broadening of nuclear magnetic resonance lines of other nuclei because of the relaxation of the nuclear spin in the changing local fields of the paramagnetic ion. It is possible to measure lifetimes of states from such line broadening measurements.

Wertz[10] has measured the broadening of the Cl^{35} resonance by several paramagnetic ions. Ferric ion produced a very large broadening effect, whereas chromic ion at the same concentration produced no observable broadening. Since chromic chloride complexes form and dissociate only very slowly, it is inferred from the above results that the rapid relaxation caused by ferric ion must be occurring almost entirely in the first coördination sphere. One can then deduce that the relaxation rate of the chlorine nucleus

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[7] E. L. King and K. Gallagher, private communication.

[8] The same type of assumption was made in references 2, 5 and 6.

[9] Although these differences are within the limits of uncertainty of the individual entropies, they are believed to be significant when considered together. The large uncertainty in the individual values arises from the resolution of the rate data into two separate rate constants.

[10] J. E. Wertz, *J. Chem. Phys.*, **24**, 484 (1956).

is equal to or less than the rate at which chloride ion enters the first coördination sphere of ferric ion.

The broadening of the full width between maxima on the derivative of the absorption curve of Cl^{35} in 3.0 M sodium chloride containing 0.1 M ferric ion was measured to be $\Delta\lambda = 1.4 \times 10^3$ sec.$^{-1}$ at 9600 gauss. Using the expression[11]

$$T_2 = \frac{1}{\sqrt{3}\pi\Delta\nu}$$

one calculates the transverse relaxation time to be 1.3×10^{-4} sec. Presumably this is an upper limit[12,13] to the lifetime of an uncomplexed chloride ion before it becomes complexed by ferric ion in the solution.

From Gamlen and Jordan's[14] data it is estimated that in 3 M Cl^- the complexes present are approximately: 10% $FeCl^{++}$, 30% $FeCl_2^+$ and 60% $FeCl_3$. Under these conditions it seems reasonable to hypothesize that the principal mechanism for entry of chloride ions into the first coordination sphere of the iron will be

$$FeCl_2^+ + Cl^- \xrightarrow{k'} FeCl_3$$

and the upper limit for the rate of randomization of nuclear spin configurations will be

$$-\frac{d(Cl^{-*})}{dt} = k'(Cl^{-*})(FeCl_2^+) = k(Cl^{-*})$$

where the asterisk indicates a particular spin configuration. Therefore

$$k' = \frac{k}{(FeCl_2^+)} \geq \frac{1}{T_2(FeCl_2^+)} = 3 \times 10^5\ M^{-1}\ \text{sec.}^{-1}$$

In the spectrophotometric study these rate constants were measured

$$Fe^{+++} + Cl^- \xrightarrow{k_1} FeCl^{++} \qquad k_1 = 9.4\ M^{-1}\ \text{sec.}^{-1}$$

$$FeOH^{++} + Cl^- \xrightarrow{k_3} FeOHCl^+ \quad k_3 = 1.1 \times 10^4\ M^{-1}\ \text{sec.}^{-1}$$

On the basis of the hydroxide catalysis of the first ferric chloride complex formation, one would expect the presence of chloride on the ferric ion to catalyze further chloride addition also, and therefore the second-order rate constant for formation of higher complexes would be greater than k_1. That k' is at least *ca.* 30-fold greater than k_3 may be plausible, but it is also possible that the next higher complex is involved, *i.e.*, the chloride ions exchange on the iron by addition of Cl^- to $FeCl_3$ to form $FeCl_4^-$. It is unfortunate that the n.m.r. measurements are not sensitive enough to detect the relaxation where only the first complex is important.

Experimental

Apparatus and Procedure.—All experimental apparatus and procedures involving the fast mixing device were identical to those reported in the earlier ferric thiocyanate study.[1] In the present work, only the box type baffle was used. Since the earlier experiments, it has been learned that bubble formation is not caused by the presence of dissolved gases in the reactants but rather by the presence of gas pockets trapped on the mixer surfaces. Two types of experiments were carried out to demonstrate this effect. First, outgassed solutions were put into the dried mixer by gravitational flow, the mixer being at one atmosphere pressure. When fired, extreme bubble formation was observed, indicating that wall effects were very important. The next step was to attempt the elimination of such effects by filling the mixer under vacuum with previously outgassed solutions, *i.e.*, by the normal filling operation used in the kinetic studies. This mode of filling is known to eliminate bubble formation. Once the mixer was filled, water saturated with air was forced in at the bottom of the mixer, displacing the outgassed water which was taken out at the top of the mixer. Care was taken that no bubbles entered the mixer. The introduction of air-saturated water was continued until several times the volume of the mixer had been displaced at the top. The bulk of the water inside the mixer was now air-saturated and no bubbles had been introduced. When the mixer was fired no bubble formation was observed, thereby demonstrating that bubble formation is not due to dissolved gases. This result does not immediately show a new method for avoiding bubble formation. The filling process described in the experiment above is not practical and in actual kinetic runs it seems probable that vacuum filling with outgassed solutions will continue to be used. It might be possible to coat the walls in such a way as to eliminate bubble trapping.

Reagents.—All reagents were prepared by methods identical to those used in the ferric thiocyanate study,[1] with the exception of the sodium chloride solution. Stock solutions of approximately 0.3 M sodium chloride were prepared by weight from the dried analytical reagent salt and checked by gravimetric analysis.

Analytical Procedures.—The extent of reaction was determined spectrophotometrically as a function of time from the oscilloscope trace. The quantity log $[(FeCl^{++})_\infty - (FeCl^{++})]$ (see Interpretation of Rate Data) equals log $[\log(x_b/x_\infty) - \log(x_b/x)]$ where x_b, x_∞ and x are the linear displacements on the oscilloscope of the blank, sample at infinite time, and sample, respectively, relative to the dark current.[1] Although no further experimental data were necessary in order to calculate k, it was desirable to check the experimental conditions. After each run a sample was removed from the mixing apparatus. The optical density of this sample was measured on a Cary spectrophotometer and this value then was compared with the value calculated from the trace on the oscilloscope of the kinetic run. The agreement was in general good to about 5% and this was taken as evidence that the sample removed was a good measure of the final equilibrium state of the sample observed kinetically during the run.

A portion of the removed sample was analyzed for total Fe(III) by adding excess sodium thiocyanate and observing the spectrum.[1] From the known total Fe(III) and the known initial concentration in the ferric solution a mixing ratio was calculated, and in turn the total (Cl^-) was obtained. Using the total Fe(III) and Cl^- concentrations and the equilibrium quotients for hydrolysis, dimerization and complexing, the concentrations of Fe^{+++}, $FeOH^{++}$, $Fe_2(OH)_2^{+4}$ and $FeCl^{++}$ were calculated. From these and the previously measured molar extinction coefficients (Table IV), the total optical density of the sample was obtained and compared with that measured on the Cary. This comparison was generally good to about 5%, indicating that the sample composition was that expected.

Molar Extinction Coefficients.—In checking the concentrations of the kinetic runs, it was necessary to know the molar extinction coefficients of all species present in the reacting solutions. Rabinowitch and Stockmayer's[2] spectrophotometric study was primarily at wave lengths above 400 mμ. Because of the low absorption of $FeCl^{++}$ above 400 mμ, it was necessary to work between 300 and 400 mμ and to determine the molar extinction coefficients in this spectral region.

Three solutions were prepared, each containing 0.003764 M $Fe(ClO_4)_3$ and each at an ionic strength of 1.15. These solutions had hydrogen ion concentrations (uncorrected for hydrolysis) of 0.250, 0.0528 and 0.0308 M. Using Milburn and Vosburgh's[4] values for Q_H and Q_D, the concentrations of Fe^{+++}, $FeOH^{++}$ and $Fe_2(OH)_2^{+4}$ were calculated. The optical densities of these solutions then were measured in 2 cm. cells on a Beckman Model DU spectrophotometer at 25

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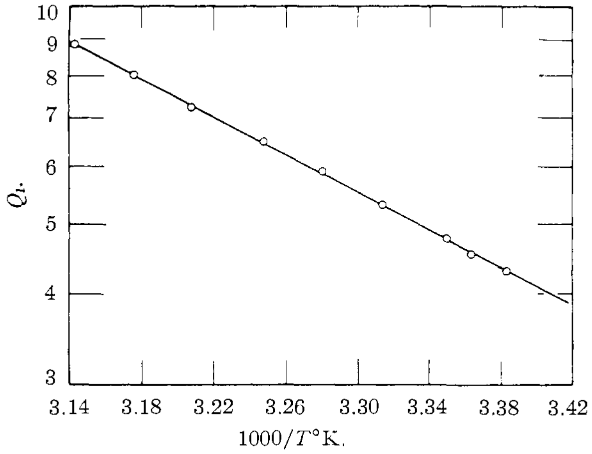

Fig. 3.—The temperature dependence of Q_1.

± 0.1°. Milburn and Vosburgh[4] had reported molar extinction coefficients for the three ferric species at 340 mμ: $\epsilon_{Fe^{+++}} = 2.84$, $\epsilon_{FeOH^{++}} = 925$ and $\epsilon_{Fe_2(OH)_2^{+4}} = 3000$. A check was made by calculating the optical density of the three solutions and comparing the results with those obtained experimentally. The results are

Solution	$\Sigma(H^+)$	D_{exp} (2.00 cm. cell)	D_{calcd}
1	0.250	0.068	0.0682
2	.0528	.276	.280
3	.0308	.512	.512

Using the calculated concentrations of Fe^{+++}, $FeOH^{++}$ and $Fe_2(OH)_2^{+4}$, and the measured optical density values for the three solutions, the molar extinction coefficients shown in columns 2, 3 and 4 in Table IV were obtained.

To obtain the molar extinction coefficients for $FeCl^{++}$ a solution identical to the high acid solution (0.250 M H^+) used above was prepared with the addition of 0.0555 M NaCl. Under these conditions, higher chloride complexes (*e.g.*, $FeCl_2^+$) are relatively unimportant. Using Rabinowitch and Stockmayer's[2] approximate value for Q_2, it is seen that the concentration of $FeCl_2^+$ is less than 5% of the concentration of $FeCl^{++}$. Neglecting the presence of $FeCl_2^+$, the measured optical density values and the calculated values of Q_H, Q_D, Q_1, $\epsilon_{Fe^{+3}}$, $\epsilon_{FeOH^{+2}}$, $\epsilon_{Fe_2(OH_2)^{+4}}$ gave the $\epsilon_{FeCl^{++}}$ values shown in column 5 of Table IV.

Although this method of obtaining the molar extinction coefficients is not highly precise, it does give a consistent set of values which may be used to check optical densities of experimental solutions. The individual values may well be in error by 10%.

Table IV

Approximate Molar Extinction Coefficients Used for Checking Concentrations

λ, mμ	$\epsilon_{Fe^{+3}}$[a]	$\epsilon_{FeOH^{+2}}$	$\epsilon_{Fe_2(OH)_2^{+4}}$	$\epsilon_{FeCl^{+2}}$[b]
390	0.61	81	1.48×10^2	2.38×10^2
380	0.63	129	4.3×10^2	4.28×10^2
370	1.00	194	1.03×10^3	7.02×10^2
360	1.59	346	1.75×10^3	1.06×10^3
350	1.97	545	2.72×10^3	1.44×10^3

[a] Milburn and Vosburgh[4] give 0.90 and 1.20 at 360 and 350 mμ, respectively. [b] Approximate values read from a graph of Olerup's data reproduced in ref. 13 are 200, 450, 750, 1000 and 1300, respectively, for the wave lengths listed.

The comparison of the values in Table IV with those reported by other workers indicates satisfactory agreement within experimental limits of error. These molar extinction coefficients were checked several times in later experiments by making known solutions and comparing experimental and calculated optical densities, with the agreement usually being within 2%.

Measurement of ΔH_1 (see equation 1).—A ferric chloride solution was prepared containing 0.01222 M $Fe(ClO_4)_3$, 0.0111 M NaCl and 1.298 M $HClO_4$, giving an ionic strength of 1.382. Equilibrium quotients for hydrolysis and dimerization of Fe(III) were calculated from the ionic strength dependence equations of Milburn and Vosburgh.[4] Using these values of $Q_H = 1.53 \times 10^{-3}$ and $Q_D = 886$ and the molar extinction coefficients previously discussed, Q_1 could be determined as a function of temperature by optical density measurements. The wave length used was 370 mμ where the total optical density due to Fe^{+++}, $FeOH^{++}$ and $Fe_2(OH)_2^{+4}$ is less than 4% of the total optical density. Furthermore, the amount of ferric hydrolyzed and complexed was very small (about 6%) and corrections on (Fe^{+++}) became almost negligible. It was assumed that the molar extinction coefficients did not change with temperature or with ionic strength.

The measurements were made on a Beckman Model DU spectrophotometer with a thermostated cell holder, using quartz cells. The temperature in the cell was held constant to ±0.1° over a temperature range from 22 to 45°. The temperatures were measured to ±0.02° with a thermistor placed inside the cell. Figure 3 shows a plot of log Q_1 *versus* 1000/T°K. The data fall on a straight line, the slope of which gives $\Delta H_1 = 6.0 \pm 0.1$ kcal./mole.

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Berkeley, California

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Variation of the Latent Heat of the Cubic–Tetragonal Transformation in the System $KNbO_3$–$KTaO_3$

By John J. Hall and Sol Triebwasser

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Measurements of the latent heat of transition of ceramic samples of $KTa_xNb_{(1-x)}O_3$ from the tetragonal to the cubic phase are reported for values of the parameter x ranging from 0 to 0.18. The latent heat is observed to decrease rapidly as x is increased from zero. The method of sample preparation, apparatus and experimental procedures are described briefly. On the basis of certain simplifying assumptions, the spontaneous polarization at the ferroelectric Curie point is calculated, using the phenomenological theory proposed by Devonshire.

Introduction

The system $KNbO_3$–$KTaO_3$ forms a continuous range of solid solutions in which the temperature of transformation from the cubic (paraelectric) phase to the tetragonal (ferroelectric) phase varies from about 680°K. for pure $KNbO_3$ to 13°K. for pure $KTaO_3$. The phase diagram of the system (which we shall write $KTa_xNb_{(1-x)}O_3$) has been studied previously[1] and the ferroelectric behavior described.[2] The purpose of the present work is to de-

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