

Stability of the Monochloroiron(III) Cation in Aqueous Solutions between 298 and 398 K

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Abstract

Equilibrium constants for the reaction $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{Cl}^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ were determined as a function of temperature over the range 298 to 398 K. As predicted by temperature corrected Pourbaix pH–potential diagrams and subsequently shown experimentally, this corresponds to the entire temperature range of stability of the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion in 1 M HClO_4 . The equilibrium constants were subjected to a van't Hoff analysis from which the enthalpy of reaction at ionic strength of 1 was estimated at $5.8 \pm 0.2 \text{ kcal mol}^{-1}$. The entropy of reaction at ionic strength 1 is estimated at $21.1 \pm 0.7 \text{ cal mol}^{-1} \text{ K}^{-1}$. The excellent fit of the van't Hoff plot (correlation coefficient 0.990) for 11 independently determined equilibrium constants over a 100 degree temperature range, suggests that throughout the Pourbaix 'region of stability' for the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion, the formation of the monochloroiron(III) cation obeys a simple thermodynamic model.

Introduction

The corrosive properties of high purity water at temperatures and pressures required for high thermodynamic efficiency has been established [1, 2]. The geochemical literature offers abundant examples of both theoretical [3] and experimental [4] studies of concentrated aqueous salt solutions at high temperature and pressure. On the other hand, chemical details of even simple aqueous reactions in dilute solutions and at high temperatures have not been studied experimentally. Based on previous studies [5], the limiting chemistry of the sub-critical boiling water steam turbine cycle is determined by the redox chemistry of the materials of construction and by the high temperature chemistry of water. Even if boiler feed water is maintained at 10^{-4} ohm^{-1} and 10 ppb or less dissolved oxygen (*i.e.* essentially free of ionic impurities and of dissolved oxygen), the principal

corrosion product is magnetite, Fe_3O_4 [6]. Repression of the formation of this product in the presence of reducing agents and in slightly acidic media ($\text{pH} < 7$) suggests that the ferrous construction materials are the source of iron and water is the source of oxygen in the Fe_3O_4 scale [7].

Among the problems which have not been explored experimentally in dilute high temperature aqueous solutions are the effects of the medium at elevated temperatures on (a) dissociation equilibria; (b) redox potentials; (c) solubilities; and (d) the stability of solute species such as ligands and metal complexes.

In this report, we will describe an experimental study of the monochloroiron(III) cation, undertaken to assess the effects of extreme temperature on the stability of a transition metal complex in aqueous solution. We have included the results of Pourbaix calculations germane to the system under study, and a detailed description of our experimental materials and procedures.

Experimental

Instrumentation

Our cell is based on a design described by Alexander *et al.* [8]. This multicomponent design has the advantage of containing a solution at the saturation pressure in contact with only fluorocarbon and the window material. Contamination of corrosive solutions by materials of construction is thereby minimized. A disadvantage arises from the fluorocarbon components which are dimensionally unstable at temperatures above about 558 K and can be used only once at the highest temperatures. A pressure jacket of stainless steel also maintains the cell within 1% of its room temperature dimensions throughout the design temperature range.

Cell Design

For clarity, we will describe the cell assembly from the inside outward. The inner cell assembly is shown in Fig. 1.

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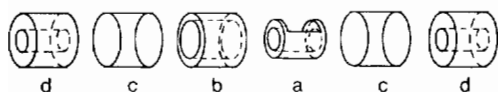


Fig. 1. High temperature cell assembly (inner part).

The fluorocarbon cell body is made up of two parts, a core (a) and a sleeve (b). The overall dimensions of the core are 10.64 mm long, 4.76 mm ID and 8.189 mm OD. The core is designed to provide enough 'head space' to allow for a liquid/vapor equilibrium at the working temperature of the solution, assuring that pressures do not exceed the saturation pressure of the solution. This is done by cutting out a section of the cylindrical core in the center at the top as shown in Fig. 1a. This section is cut so that 1.59 mm of the core is left at both ends for support. The head space has a volume of 0.06 ml. The dimensions of the sleeve are 10.64 mm long, 10.16 mm OD and 8.13 mm ID.

The windows (c) are 10.0 mm thick by 10.0 mm diameter synthetic sapphire cylinders (Union Carbide) which are inert to the test solutions and can withstand the pressures (200–300 bar) of aqueous solutions at the design temperature of 603 K.

Copper thrust rings (d) are placed behind each window align the windows and give a tight seal (Fig. 1). Copper was chosen to provide for slight deformation as required to compensate for thermal expansion of metal components of the cell assembly. The thrust rings are cylindrical with length 10.44 mm, 10.0 mm OD and 4.76 mm ID.

When assembled, the fluorocarbon cell body is under slight compression between sapphire windows each followed by the copper thrust rings. These parts are then enclosed between two halves of a thin longitudinally split stainless steel cylinder. This component provides a structure which may be pressed to insert or remove the inner fluorocarbon cell and windows from the outer pressure jacket without risk to the windows. These parts comprise the inner cell assembly which is then placed inside the outer stainless steel pressure jacket.

The fully assembled cell and pressure jacket has an outside diameter of 25.2 mm and a length of 101.6 mm. Two gland nuts are threaded against the copper thrust rings to compress the inner cell assembly against the sapphire windows for a leak-proof seal. Thus, the solution is in contact with only fluorocarbon and the sapphire windows.

The cells were heated in a 50.8 × 76.2 × 101.6 mm block machined from aluminum. Two holes, 25.4 mm in diameter, were drilled longitudinally to be used for the sample and reference cells. Holes were also drilled for the insertion of up to ten 100 W stainless steel heating elements (0.375" d × 2" l) at various positions inside the block. Twelve 0.068 inch holes were drilled in the block for thermocouple sensors.

The temperature of the cell was controlled by an Omega Model 4001 indicator controller fitted with a type K thermocouple. This device has a range of 270–773 K with control to 1° and adjustable proportional heating and dead band which we optimized with the heating block containing the stainless steel pressure jackets.

In a series of preliminary experiments, we heated the block to the maximum design temperature (603 K) on a bench top. We found that four 100 W cartridge heaters heat the block to 603 K in less than 20 min. We moved the thermocouple to various locations in the heater block, to establish that the temperature of the block varied by no more than 1° among test locations, and that the temperature within the cell cavity was within 4° of that of the aluminum block. Temperature regulation, which we estimated from the time required to achieve equal on and off duty cycles of the regulator, was established within 5 min at all temperatures.

All spectrophotometric data were obtained with a Cary model 14R spectrophotometer. We bolted a heat sink constructed from a 7 × 9 × 3/32 inch plate of copper to which one meter of 1/4 inch copper tube was soldered to the outside of the spectrophotometer cell compartment. Tap water circulating within the heat sink maintained the temperature of the spectrophotometer at or below 303 K for any temperature of the aluminum heater, up to the design temperature of 603 K.

Sample Preparation

Ferric perchlorate was prepared by dissolution of 20 g (0.36 mol) 99.9% reagent grade iron wire in 150 ml 9.5 M HClO₄ (1.43 mol) at 333 K for one hour followed by recrystallization of the ferric salt. The salt was then dissolved in 1 M HClO₄ and the iron quantitated by the method of Sutin *et al.* [9]. Stock solutions of HCl and HClO₄ were prepared and quantitated by titration against NaOH standardized with potassium biphthalate.

The spectrophotometer cell was filled with the test solution by first assembling the inner cell with the fluorocarbon insert, one window and one thrust ring. This was then loaded into the outer core and one gland nut screwed into place. The cell was placed on end and filled with a 2 ml microburet. After the desired volume was placed in the cell, the second window and copper spacer were put into place followed by the second nut which was tightened to give a leak proof seal between the windows and fluorocarbon.

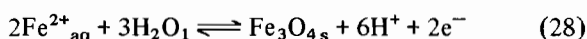
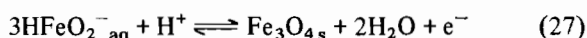
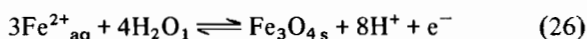
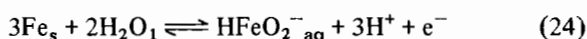
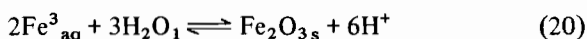
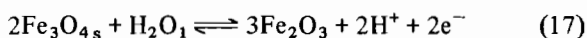
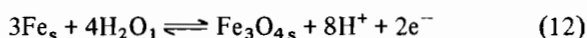
For each concentration of Fe³⁺, a complete temperature profile (298 to 398 K) was performed on a single sample. Following temperature equilibration, the spectrum was scanned from 500 nm to a short wavelength limit where the absorbance exceeded 2.

Absorbance data were read from the Cary 14 strip chart. Three separate runs were made for each Fe^{3+} concentration.

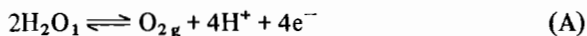
Results and Discussion

Pourbaix Calculations

Pourbaix [10] described pure metallic iron in the presence of water in terms of a limited number of half reactions. Some of the oxidation reactions are listed below with the numbers originally given to the reactions given by Pourbaix



Pourbaix considered only two reduction half reactions involving solvent



to complete the electrochemical process. We chose parameters which are drawn from the work of Criss and Cobble [11] and standard references [12–14]. Details of the calculations, which entail a relatively straightforward application of thermodynamics, are given elsewhere [15].

The horizontal lines on Pourbaix diagrams (Figs. 2–5) correspond to the defining reactions which have no pH dependence, and vertical lines indicate an equilibrium at a particular pH which involves no redox chemistry. The temperature dependence of the equilibrium $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} \rightleftharpoons \text{Fe}_2\text{O}_3$ is particularly interesting. This is the reaction which results in the familiar hydrated iron oxide or ‘rust’ at $\text{pH} > 2$ at room temperature. As temperature is increased, the pH at which $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is stable relative to Fe_2O_3 shifts to values < 0 at temperatures above about 423 K. We have discussed other details elsewhere [15].

Equilibrium Studies

Several worthwhile observations emerged from preliminary studies we performed to establish the

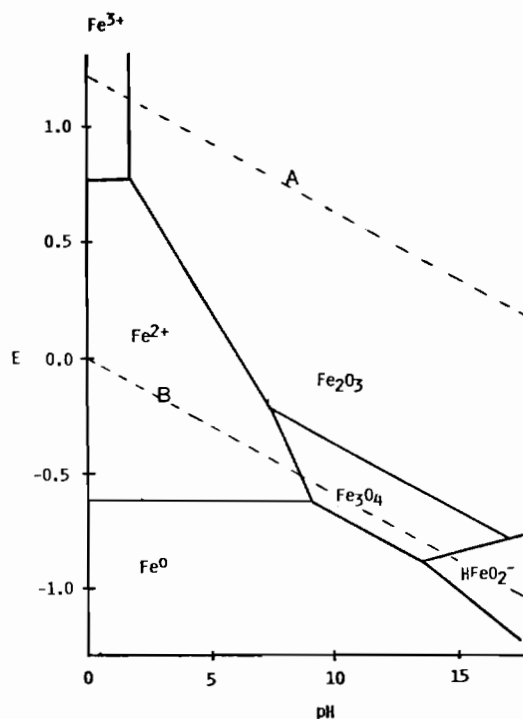


Fig. 2. Iron–water pH–potential diagram at 298 K.

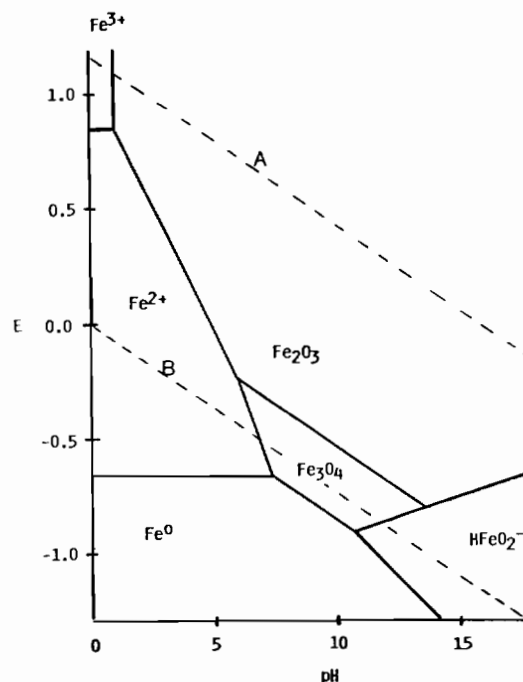


Fig. 3. Iron–water pH–potential diagram at 373 K.

conditions under which the planned experimental protocol would produce interpretable results.

We found, in accord with Sutin *et al.* [9], that commercial reagent grade perchloric acid contains

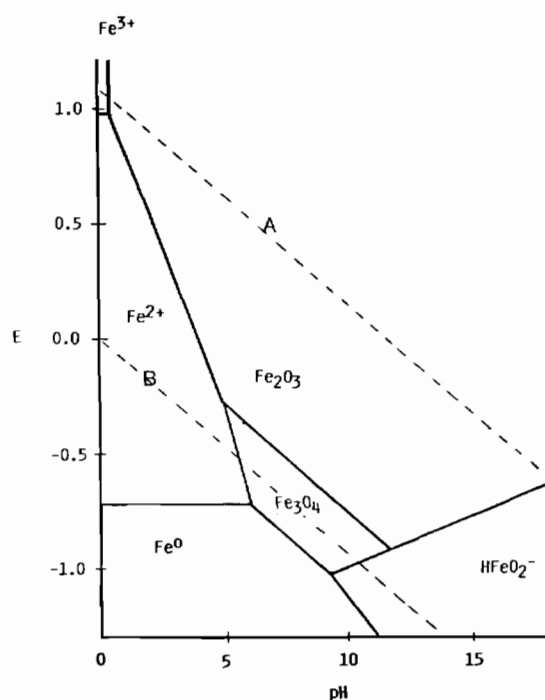


Fig. 4. Iron-water pH-potential diagram at 473 K.

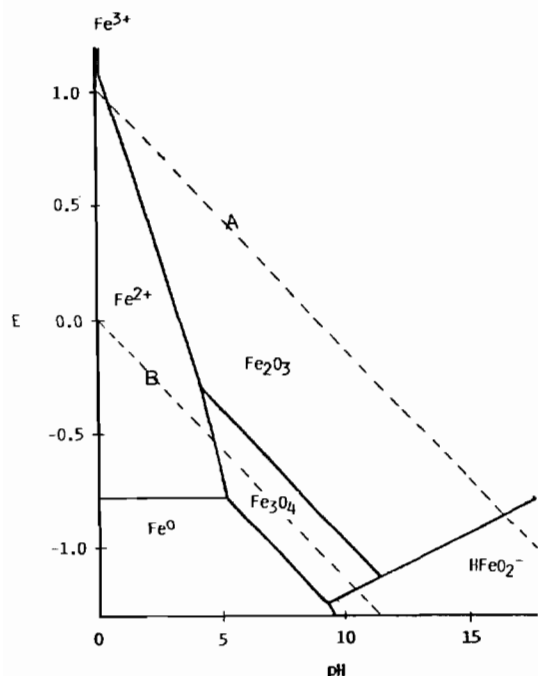


Fig. 5. Iron-water pH-potential diagram at 573 K.

sufficient chloride to perturb the electronic spectrum of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. Fuming a fresh supply of HClO_4 at 80°C for about 1 h sufficed to reduce the level of chloride below detection limits.

We also found the preparation of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ solutions to be surprisingly dependent on conditions. From time to time, preparations would be yellow rather than pale violet. We are hesitant to use large quantities of potentially hazardous perchlorates, and the temperatures of small volumes are not closely controlled on commercial hotplates (Corning PC351, in our case). Nonetheless, we found that careful cleaning of the glassware and careful monitoring of the heating and reaction time yielded $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ reproducibly.

We tested the high temperature cell assembly with pure water and perchloric acid solutions over the temperature range 298 to 603 K to find operating parameters which gave acceptable performance. We found that solutions of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ in the presence of variable amounts of HCl produced non-linear and often discontinuous and irreversible increases in optical density at temperatures above 423 K. We traced this phenomenon to a red deposit on the interior of the cell and windows. While we did not identify the product, the precipitation of Fe_2O_3 is consistent with Pourbaix calculations which indicate that $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is unstable relative to Fe_2O_3 at pH 0 and a temperature near 433 K. Accordingly, we conducted all of our experiments between 298 and 398 K.

All of our equilibrium data were collected at ionic strength 1, and no corrections were applied for the small negative temperature coefficient of ionic strength [16]. Our data were collected at the saturation pressure of the solution. Following Helgeson [16], we considered pressure effects to be negligible up to the critical point.

The concentration of species at equilibrium in solutions containing *ca.* 10^{-2} M Fe^{3+} and 10^{-3} M Cl^- in 1 M HClO_4 were determined spectrophotometrically as a function of temperature over the range 298 to 398 K.

Following the method of Sutin *et al.* [9], concentrations were determined at three different wavelengths to assure that unique species were observed under each set of experimental conditions. The experimental data appear in Table 1. The variation in observation wavelength with temperature was necessitated by the increased absorbance of the samples. Concentrations were chosen to give reproducible absorbance measurements under conditions of minimum absorbance (298 K), and spectra were scanned at the specified temperatures. There are no isosbestic points in the spectra, but the absorbancies obey the Beer-Lambert law at the chosen wavelengths and at any temperature with linear correlation coefficients for both Fe^{3+} and FeCl^{2+} above 0.97 and intercepts of 0 (within 3 standard deviations).

The hydrolysis constant for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} = [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}^+$ is approximately 10^{-2} [9].

TABLE 1. Equilibrium Absorbance Data for the System $[\text{Fe}^{3+}]_{\text{aq}} + \text{Cl}^- \rightleftharpoons [\text{FeCl}^{2+}]_{\text{aq}}$

[Fe ³⁺] (mol/l)	Absorbance, T = 298 K					
	340 nm		350 nm		360 nm	
	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺
0.0354	0.169	0.870	0.096	0.704	0.070	0.525
0.0283	0.143	0.724	0.087	0.579	0.068	0.432
0.0212	0.113	0.568	0.074	0.458	0.056	0.339
0.0177	0.073	0.502	0.044	0.409	0.032	0.306
0.0141	0.068	0.378	0.038	0.304	0.025	0.226
	Absorbance, T = 323 K					
	340 nm		350 nm		360 nm	
	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺
0.0354	0.375	1.605	0.234	1.325	0.156	0.985
0.0283	0.318	1.366	0.204	1.127	0.140	0.852
0.0212	0.239	1.045	0.154	0.866	0.106	0.658
0.0177	0.182	0.928	0.110	0.770	0.072	0.587
0.0141	0.167	0.718	0.107	0.599	0.062	0.459
	Absorbance, T = 348 K					
	360 nm		370 nm		380 nm	
	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺
0.0345	0.388	1.802	0.239	1.267	0.140	0.827
0.0283	0.321	1.534	0.204	1.084	0.126	0.692
0.0212	0.242	1.220	0.155	0.865	0.094	0.560
0.0177	0.185	1.085	0.117	0.770	0.070	0.505
0.0141	0.150	0.835	0.093	0.587	0.060	0.382
	Absorbance, T = 373 K					
	380 nm		390 nm		400 nm	
	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺
0.0354	0.386	1.508	0.237	0.968	0.147	0.588
0.0283	0.307	1.253	0.192	0.813	0.120	0.501
0.0212	0.231	1.013	0.146	0.648	0.091	0.405
0.0177	0.182	1.085	0.117	0.770	0.070	0.505
0.0141	0.145	0.759	0.091	0.480	0.059	0.292
	Absorbance, T = 398 K					
	390 nm		400 nm		410 nm	
	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺	Fe ³⁺	FeCl ²⁺
0.0354	0.569	1.673	0.356	1.058	0.227	0.653
0.0283	0.447	1.457	0.283	0.918	0.178	0.565
0.0212	0.326	1.220	0.204	0.760	0.143	0.470
0.0177	0.258	1.055	0.171	0.672	0.109	0.410
0.0141	0.209	0.872	0.134	0.447	0.089	0.333

Thus, at pH 0 and 298 K, the concentration of $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ is less than 1% of the total iron. Based on these data and our observation that the

absorbancies of both Fe^{3+} and FeCl^{2+} conform to the Beer–Lambert law, we have ignored absorption by $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ in the equilibrium concentration calculations.

In a variable excess of $[\text{Fe}^{3+}]_{\text{aq}}$ over $[\text{Cl}^-]$ and at a pH sufficiently low (0, 1 M HClO_4) to suppress the hydrolysis of $[\text{Fe}^{3+}]_{\text{aq}}$, equilibrium constants were calculated from the spectrophotometric data using the linear expression of Sutin *et al.* [9]

$$[\text{Fe}^{3+}]_{\text{aq}}[\text{Cl}^-]_{\text{total}}/\Delta A[\text{Fe}^{3+}] = 1/e_1K_1 + [\text{Fe}^{3+}]/e_1$$

where $\Delta A[\text{Fe}^{3+}]$ is the difference in absorbance between the $[\text{Fe}^{3+}]_{\text{aq}}$ and the corresponding $[\text{FeCl}^{2+}]$ solutions of Table 1, and e_1 is the molar extinction coefficient, from which the equilibrium constant is given by the ratio of the slope to the intercept eliminating the need to evaluate the molar extinction coefficient of the species under each set of conditions. The equilibrium constants are given in Table 2, with errors estimated from the linear least-squares and correlation methods. Of the fifteen determinations, four were shown statistically to lie outside of the limits of error. These 'outliers' did not define any trend in temperature or observation wavelength.

The equilibrium constants were subjected to a van't Hoff analysis from which the enthalpy of reaction at ionic strength of 1 was estimated at $5.8 \pm 0.2 \text{ kcal mol}^{-1}$, in reasonable agreement with Sutin's estimate of $5.0 \text{ kcal mol}^{-1}$. The entropy of reaction at ionic strength 1 is estimated at $21.1 \pm 0.7 \text{ cal mol}^{-1} \text{ K}^{-1}$, also in good agreement with Sutin's estimate of $24 \text{ cal mol}^{-1} \text{ K}^{-1}$.

In the present study, equilibrium constants for the reaction $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{Cl}^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ were determined as a function of temperature over the range 298 to 398 K. As predicted by temperature corrected Pourbaix pH–potential diagrams and subsequently shown experimentally, this corresponds to the entire temperature range of stability of the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion in 1 M HClO_4 .

Our equilibrium constants and thermodynamic constants are in excellent agreement with those which Sutin obtained over a 20 degree temperature span at about room temperature. The excellent fit of the van't Hoff plot (correlation coefficient 0.990) for 11 independently determined equilibrium constants over a 100 degree temperature range, suggests that throughout the Pourbaix 'region of stability' for the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion, the formation of the monochloroiron(III) cation obeys a simple thermodynamic model.

Acknowledgements

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TABLE 2. Temperature Dependence of the Equilibrium Constants for the Reaction $[\text{Fe}^{3+}]_{\text{aq}} + \text{Cl}^- \rightleftharpoons [\text{FeCl}^{2+}]$

At 298 K		
$K_{340} = 5.78 \pm 0.62$	$K_{350} = 5.08 \pm 0.28$	$K_{360} = 5.47 \pm 0.20$
At 323 K		
$K_{340} = 6.20 \pm 0.46$	$K_{350} = 6.61 \pm 0.25$	$K_{360} = 10.37 \pm 0.50$
At 348 K		
$K_{360} = 12.14 \pm 0.36$	$K_{370} = 11.58 \pm 0.60$	$K_{380} = 10.29 \pm 0.86$
At 373 K		
$K_{380} = 22.33 \pm 0.74$	$K_{390} = 19.28 \pm 1.72$	$K_{400} = 19.55 \pm 0.38$
At 398 K		
$K_{390} = 38.34 \pm 0.88$	$K_{400} = 34.62 \pm 1.89$	$K_{410} = 29.37 \pm 1.53$

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