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Molar Absorptivities in the Ultraviolet and Visible Ranges for Gas-Phase Monomeric and Dimeric Iron(III) Chloride, Vapor Pressure of Solid Iron(III) Chloride, and Equilibrium between Monomeric and Dimeric Iron(III) Chloride

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Temperature-dependent equations for molar absorptivities at 10-nm intervals from 240 to 480 nm for $Fe_2Cl_6(g)$ between 465 and 727 K and $FeCl_3(g)$ between 678 and 887 K are reported. Results at 360 nm were used to recalculate vapor pressures of $FeCl_3(s)$ from previously reported absorbance data. These vapor pressures, when combined with the results of other investigators, give the relationship $\ln [P\ (\mathrm{atm})] = 29.69(\ln T) - 0.06472T + (1.85 \times 10^{-5})T^2 - 12613/T - 136.15$ for the equilibrium $2FeCl_3(s) = Fe_2Cl_6(g)$ from 425 to 575 K. Equilibrium constants for the reaction $Fe_2Cl_6(g) = 2FeCl_3(g)$ from 812 to 932 K have been derived from total pressures measured in a quartz diaphragm gauge.

Introduction

In two previous papers,[1,2] the molar absorptivities for monomeric, $FeCl_3(g)$, and dimeric iron(III) chloride, $Fe_2Cl_6(g)$, at wavelengths between 200 and 480 nm and at temperatures between 473 and 923 K were reported. Later,[3] these molar absorptivities were used to derive vapor pressures of solid iron(III) chloride from absorbance measurements at various temperatures. The resulting vapor pressures were ca. 20% higher than those based on studies using other methods.

In a similar study, the calculated molar absorptivities for iron(II) chloride were higher when hydrogen chloride was added to the quartz absorption cell.[4] The hydrogen chloride prevents interaction of the iron(II) chloride with OH and H_2O groups on the surface of the quartz. This interaction reduces the amount of iron(II) chloride in the vapor phase. We now find a similar effect for iron(III) chloride at relatively higher concentrations of hydrogen chloride and report a new determination of the molar absorptivities for monomeric and dimeric iron(III) chloride. The newly derived values are higher than those reported previously and lead to vapor pressures in good agreement with those based on other methods.

The concentrations of monomer and dimer in the vapor mixtures are derived from the total amount of iron present and equilibrium constants for reaction 1. Literature values[5] for these constants

$$Fe_2Cl_6(g) = 2FeCl_3(g) \qquad (1)$$

are based on two studies in which contamination might have occurred. In the first study, the dissociation was studied in conjunction with the reaction of iron(III) oxide with hydrogen chloride. Because water is also produced in this reaction, $Fe(H_2O)Cl_3(g)$ might have formed.[6,7] In the second study, a molten sodium chloride manometer was used and, thus, the formation[2] of $NaFeCl_4(g)$ is expected. Consequently, we made an independent determination of the equilibrium constants for the dimer–monomer equilibrium in a mixture of iron(III) chloride, chlorine, and hydrogen chloride using a quartz diaphragm gauge.

Experimental Section

Dimer–Monomer Equilibrium. A 19.05-mL quartz diaphragm gauge[8] containing 7.7 mg of iron wire (Allied Chemical, 99.90%) was evacuated and flamed. Chlorine gas, vaporized off excess liquid chlorine that had been generated by the thermal decomposition of anhydrous copper(II) chloride, was admitted into the gauge. An excess of chlorine was left in the gauge, after complete reaction of the iron wire, and its pressure was measured. Hydrogen chloride (Matheson) was vaporized off excess liquid hydrogen chloride. The gas was then passed through a dry-ice trap and condensed into the gauge, cooled with liquid nitrogen. Then, the gauge was sealed off from the vacuum line. The pressures of chlorine and hydrogen chloride in the gauge at 300 K were 20 and 164 Torr, respectively.

The gauge was heated in a tube furnace; temperatures were measured with chromel–alumel thermocouples positioned at the middle and bottom of the gauge. The temperature difference between the two positions was kept less than 6 K. Cooling the gauge slowly after complete vaporization of the iron(III) chloride resulted in the uniform deposition of crystals inside the gauge, indicating no significant temperature gradient. The temperature at the middle of the gauge was taken as the temperature of the gas in the gauge.

Molar Absorptivities. The experimental procedures for the preparation of the samples have been described previously,[1-3] and only a summary is given here.

A quartz absorption cell (1.9 cm i.d., 1–10 cm path length) was connected, through a long quartz side arm with several alternating 2 mm i.d. and 4 mm i.d. sections, to a high-vacuum line. A small piece of iron wire was introduced into the quartz side arm. After the cell was flamed under high vacuum, an excess of chlorine, obtained as above, was admitted into the cell and the mixture flamed to produce iron(III) chloride. A small part of the iron(III) chloride was sublimed into the cell, and some excess chlorine was condensed in the cell, cooled with liquid nitrogen. Then one of the small-bore quartz sections of the side arm was sealed off. The chlorine concentration was determined from the absorbance at 330 nm at room temperature.

The cell was heated, and spectra were recorded with a Cary 14H spectrophotometer. The absorbances of the iron(III) chloride vapor at various wavelengths and temperatures were derived from the total absorbance by subtracting the corresponding chlorine absorbances.

After these measurements, the cell side arm was reconnected to the vacuum system in order to add hydrogen chloride. A 4 mm bore section of the side arm of the cell was slipped into a tight-fitting Pyrex ball joint and sealed to the adjoining tube with black vacuum wax. A smaller bore section of the side arm, scratched with a file near the ball joint, extended through the joint into the matching half that was attached to the vacuum line. After evacuation of the assembly and condensation of the chlorine and iron(III) chloride in the cell body, the tip was cracked off by slightly tilting the halves of the joint. A manometrically measured amount of hydrogen chloride, pretreated as above, was then condensed into the cell. The side arm was again sealed, the cell was reheated, and spectra were recorded.

If a trace of water was transported with the HCl and Cl_2 into the cell, a thin, reddish golden film of iron(III) chloride in the cell would become colorless upon vaporization of the gases at room temperature and reddish golden again upon condensation of the gases with liquid nitrogen.[7] In two samples such color changes did occur. To eliminate the trace of water in each of these samples, the gases were condensed in the tip of the side arm of the cell with a liquid-nitrogen bath. Then, the gases were allowed to vaporize slowly until the temperature of the tip reached about that of dry ice, at which time dry ice was placed around the tip and the

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Table I. Temperatures[a] and Pressures[b] for Equilibrium Mixtures of $Fe_2Cl_6(g)$ and $FeCl_3(g)$ Measured in a Quartz Diaphragm Gauge

T, K	P_T, Torr	P_M, Torr	P_D, Torr
812	696	41.2	160.8
840	726	54.6	160.4
848	736	61.3	158.8
854	740	59.3	161.1
861	750	67.6	158.5
878	774	87.4	152.5
882	776	84.7	154.7
893	790	94.4	152.3
899	798	100.4	150.6
919	826	123.2	143.7
932	838	125.5	145.4
893	798	110.4	144.3
880	778	92.0	150.6
859	752	75.0	154.4
845	734	62.3	157.6
866	752	63.3	161.8
819	702	41.5	162.2

[a] Estimated uncertainty is ±1 K. [b] Standard deviation for a given P_T value is ±1 Torr, and the propagated standard deviations for P_M and P_D are ±2 and ±3 Torr, respectively.

Table II. Molar Absorptivity (L mol^{-1} cm^{-1})–Temperature (K) Equations, $\epsilon = \boldsymbol{A} + \boldsymbol{B}T$, for $Fe_2Cl_6(g)$ and $FeCl_3(g)$[a]

λ,	$\epsilon_{Fe_2Cl_6(g)}$ (465–727 K)		$\epsilon_{FeCl_3(g)}$ (678–887 K)		av rel
nm	$10^{-3}\boldsymbol{A}$	$\boldsymbol{B}$	$10^{-3}\boldsymbol{A}$	$\boldsymbol{B}$	diff,[b] %
240	14.09	−4.91	5.48	−4.07	2.0
245	14.72	−5.20	5.81	−3.76	1.6
250	13.73	−3.77	7.33	−4.75	1.6
260	10.80	−0.52	7.91	−4.57	1.6
270	8.89	+0.84	6.86	−3.62	1.7
280	7.38	+1.75	5.50	−2.66	1.5
290	5.14	+3.65	3.24	−0.46	1.3
300	3.73	+4.23	3.00	−0.08	1.0
310	3.32	+3.95	3.60	−0.04	1.2
320	3.54	+3.81	4.59	−0.06	1.2
330	5.60	+1.84	6.89	−1.50	1.1
340	9.44	−1.69	8.34	−2.22	1.2
350	13.93	−6.15	8.96	−2.50	1.2
360	15.50	−7.03	7.66	−1.16	1.3
370	14.13	−5.23	6.30	−0.19	1.1
380	10.61	−1.55	5.08	+0.34	1.1
390	6.71	+2.06	3.69	+0.95	1.2
400	3.26	+5.20	1.28	+2.80	1.7
410	1.24	+6.19	−0.06	+3.47	1.9
420	0.46	+5.40	0.22	+2.37	1.8
430	−0.18	+4.96	−0.21	+2.22	1.7
440	−0.63	+4.65	−0.81	+2.42	2.1
450	−0.65	+3.85	−0.86	+2.09	2.6
460	−0.43	+2.89	−0.63	+1.54	2.9
470	−0.28	+2.19	−0.47	+1.16	3.9
480	−0.28	+1.82	−0.44	+0.97	4.7

[a] Based on 34–50 absorbances at each wavelength. [b] $(\sum(|\boldsymbol{A}(\text{obsd}) - \boldsymbol{A}(\text{calcd})|)(100/\boldsymbol{A}(\text{obsd}))/(\text{no. of observns})$ where $\boldsymbol{A}(\text{calcd}) = \epsilon_D C_D + \epsilon_M C_M$.

tip was immediately sealed off, to remove the trace of water still condensed in the tip. A subsequent color test indicated that the trace of water was removed.

After completion of the absorbance measurements, the iron(III) chloride in the cell was dissolved in 2% nitric acid and the amount of iron was determined by using an ICP emission spectrometer (Model 955 Plasmo Atomcomp). The volumes of the cell and of the various lengths of the side arm were determined from the masses of water contained and the density of the water.

Results

Dimer–Monomer Equilibrium. A linear least-squares treatment of pressure vs temperature from 300 to 420 K (only HCl and Cl_2 gases present, 5 pressure readings) gave P_1 (Torr) = $0.6084T$ and from 585 to 720 K (HCl, Cl_2, and $Fe_2Cl_6(g)$ present, 11 pressure readings) gave P_2 (Torr) = $0.8318T$. The amount of iron in the gauge calculated from the difference between P_1 and P_2 is 7.6 mg, which is the same within experimental uncertainty as the weighed amount of iron (7.7 mg) placed in the gauge.

The pressures and temperatures in the range where dimer dissociation (eq 1) is important are listed in Table I. The pressures of monomer, P_M, and dimer, P_D, were calculated with use of the relationships

$$P_M = 2(P_T - P_2) \tag{2}$$

$$P_D = P_T - P_1 - P_M \tag{3}$$

where P_T is the total pressure. A least-squares treatment of ln (P_M^2/P_D) vs $1/T$, based on the equation ln $(P_M^2/P_D) = -\Delta H°/RT + \Delta S°/R$, gave $\Delta H°$ and $\Delta S°$ values of 135.6 (±6.0%) kJ/mol and 131.0 (±7.2%) J/(K mol), respectively (relative standard deviations in parentheses). Within experimental uncertainty, these values agree with those reported in ref 5 at 900 K—137.74 kJ/mol and 132.30 J/(K mol), respectively. Apparently, the formation of iron(III) chloride hydrate in the first study and of sodium tetrachloroferrate(III) in the second study did not lead to significant errors.[5] Consequently, the values in ref 5 at the various temperatures were used in the calculations of the equilibrium constants and concentrations of monomer and dimer in the absorbance samples.

Molar Absorptivities. Molar absorptivities for the monomer and dimer were calculated at temperatures of 576 K and above with use of the relationships

$$C_{Fe} = C_M + 2C_D \tag{4}$$

$$K = C_M^2RT/C_D \tag{5}$$

$$A/b = \epsilon_M C_M + \epsilon_D C_D \tag{6}$$

C_{Fe}, C_M, and C_D represent respectively the concentration equivalent (mol/L) of the total amount of iron, the concentration of monomer, and the concentration of dimer in a given sample at a given temperature. K is the equilibrium constant for the dimer–monomer equilibrium (eq 1). The values for K at the various temperatures were derived from thermodynamic data tabulated in ref 5. A, b, ϵ_M, and ϵ_D represent the absorbance at a given wavelength, the cell path length in cm, and the molar absorptivities of the monomer and dimer at the given wavelength, respectively.

Values of C_D and C_M for the various samples at a measured temperature were derived by using eq 4 and 5. Then, a least-squares treatment of $A/(bC_D)$ vs C_M/C_D (modified eq 6) at various wavelengths was carried out to obtain the corresponding molar absorptivities. The absorbances for the samples were measured at roughly 50 K intervals.[9] Below 576 K, the concentration of monomer is negligible, and the molar absorptivities for the dimer were calculated directly from A and C_D.

The concentrations of dimer between 465 and 727 K were sufficiently high to obtain reasonably precise molar absorptivities for the dimer. The variation of the molar absorptivity with temperature at each wavelength was approximated by a least-squares fit to the empirical equation $\epsilon = \boldsymbol{A} + \boldsymbol{B}T$. The derived constants $\boldsymbol{A}$ and $\boldsymbol{B}$ are listed for the various wavelengths in Table II. At temperatures above 779 K, the concentrations of monomer were sufficiently high to obtain reasonably precise molar absorptivities for the monomer and the temperature dependences of these values were also approximated by linear equations. Because the temperature range for the dimer was larger than that for the monomer, and in order to obtain more precise molar absorptivities for the monomer below 779 K, the linear equations for the dimer were used with eq 6 and the molar absorptivities for the monomer were recalculated. These recalculated absorptivities were consistent with the linear relationships derived at the higher temperatures and made it possible to extend the temperature range down to 678 K. The constants for these linear equations are given in Table II.

The concentrations of the reagents in the various spectral samples, the cell dimensions, and the temperature ranges over

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[9] Supplementary material.

Table III. Concentrations of Reagents, Cell Dimensions, and Temperature Range

sample no.	$10^5[\mathrm{FeCl_3}]$,[a] mol/L	$10^4[\mathrm{Cl_2}]$,[b] mol/L	$10^2[\mathrm{HCl}]$,[c] mol/L	b,[d] cm	vol,[e] mL	temp range, K
1	0.876 ± 0.006[f]	0.47 ± 0.03	1.62 ± 0.01	10	29.44	465–885
2	2.40 ± 0.02	0.38 ± 0.03	1.52 ± 0.01	10	30.72	492–887
3	0.871 ± 0.009	0.38 ± 0.03	1.52 ± 0.01	10	30.16	469–882
4a	4.52 ± 0.09 (4.04 ± 0.05)	2.0 ± 0.1	...	5	16.38	472–675
4b	4.71 ± 0.09	2.1 ± 0.1	1.37 ± 0.01	5	15.72	472–680
5a	2.55 ± 0.05 (2.52 ± 0.03)	0.71 ± 0.09	...	5	16.88	475–581
5b	2.67 ± 0.05	0.74 ± 0.09	2.26 ± 0.02	5	16.12	475–627
6	5.01 ± 0.08	4.1 ± 0.1	2.43 ± 0.02	5	16.46	524–579
7	17.1 ± 0.8 (16.0 ± 0.2)	13 ± 1	0.655 ± 0.005	1	4.33	575–884

[a] Based on analytical iron except for values in parentheses, which were calculated from absorbances and molar absorptivities. [b] Spectroscopically determined. [c] Manometrically determined. [d] Path length ±0.001 cm, certified by Pyrocell Manufacturing Co., Westwood, NJ. [e] Determined from mass of water necessary to fill cell. [f] All of the ± values are estimated uncertainties.

which the samples were heated are listed in Table III. In samples 4a, 5a, and 7, the concentrations of iron(III) chloride derived from analytical and spectral data are both given. In the other samples the two concentrations were the same. The spectral concentrations are based on the absorbances of the samples and the molar absorptivities for $\mathrm{Fe_2Cl_6(g)}$ from Table II at the minimum temperatures listed, where the concentrations of the monomer are negligible. The spectral concentrations of iron were used for these samples in eq 4 for the determination of molar absorptivities at higher temperatures.

Discussion

Molar Absorptivities. We found, in an earlier study,[4] that iron(II) chloride vapor reacts reversibly with $\mathrm{H_2O}$ and OH groups on the surface of the quartz absorbance cell. Consequently, some of the iron(II) chloride is removed from the vapor. The iron product on the surface is soluble in the 2% nitric acid solution used to dissolve the sample for the subsequent iron determination. Thus, molar absorptivities for $\mathrm{FeCl_2(g)}$ calculated by dividing the absorbance by the amount of analytical iron were too low. This effect decreased as the concentration of hydrogen chloride in the cell was increased to about 1×10^{-3} mol $\mathrm{L^{-1}}$. In the earlier study[3] of iron(III) chloride, addition of comparable amounts of hydrogen chloride produced no noticeable change in the derived molar absorptivities. However, in the present study, an increase of the concentration of hydrogen chloride to about 2×10^{-2} mol $\mathrm{L^{-1}}$ gave derived molar absorptivities that were larger by about 15%. Apparently, the higher partial charge on iron(III) compared to that on iron(II) causes a stronger interaction with the $\mathrm{H_2O}$ and OH groups bound to the quartz,[10] requiring a higher inhibiting concentration of hydrogen chloride.

Samples 4a and 4b in Table III show the effect of adding a sufficient amount of hydrogen chloride to inhibit the interaction with the $\mathrm{H_2O}$ and OH groups bound to the quartz. Sample 4b was prepared by adding hydrogen chloride to sample 4a. If there were no interaction with the groups in sample 4a, the spectral concentration of iron(III) chloride would have been the same as the analytical concentration. The analytical concentrations differ between a and b samples due to volume changes with sealing off the side arm.

Apparently, in sample 7 there was not enough hydrogen chloride to prevent the surface interaction because the spectral concentration of iron is lower than the analytical concentration. However, the percent difference is less than for sample 4a.

Samples 5a and 5b are related similarly as samples 4a and 4b. However, there is essentially no interaction in sample 5a. This is the only exception found in either this study or the earlier studies.[1-3] Other factors such as the roughness of the inner walls of the cell may need to be considered.

Samples 4a and 5a were heated only over narrow temperature ranges. The molar absorptivities, based on the spectral iron concentrations, for these samples matched those from the other samples, indicating that the temperature dependency of the interaction with the surface groups is not significant over the ranges used. Sample 7 values, with the added hydrogen chloride, also matched well over the much wider temperature range.

In various nonaqueous solvents at room temperature, $\mathrm{HFeCl_4}$ forms from HCl and $\mathrm{FeCl_3}$ with fairly high equilibrium constants such as 1×10^4 in isopropyl ether.[11] Because of the substantial concentrations of hydrogen chloride in some of our samples, the possible formation of $\mathrm{HFeCl_4}$ was considered. However, a vapor pressure sample containing a large amount of solid iron(III) chloride, 2.8×10^{-2} mol/L of hydrogen chloride, and 4.1×10^{-4} mol/L of chlorine showed *no* increase in absorbance compared to that of vapor pressure samples with no added hydrogen chloride. We conclude that $\mathrm{HFeCl_4(g)}$ is not present at significant concentrations in our vapor mixtures.

Further support that the only iron-containing species in the gas phase were $\mathrm{FeCl_3(g)}$ and $\mathrm{Fe_2Cl_6(g)}$ is given by an evolving factor analysis.[12] With use of absorbances for 18–22 wavelengths per sample, the samples were combined in various orders such as increasing hydrogen chloride or iron concentrations at a given temperature. The analysis showed only one or two absorbing components (dimer or dimer and monomer) present depending on the temperature in the various samples, with or without added hydrogen chloride.

Relative integrated areas were determined, with use of Simpson's one-third rule, for the spectra at various temperatures derived from the equations in Table II. The areas for the dimer are as follows (temperature, K): 15.6 (471), 15.9 (492), 16.0 (526), 15.8 (576), 15.9 (625), 15.8 (678), 16.9 (727). The areas for the monomer are as follows (temperature, K): 8.56 (678), 8.58 (727), 8.58 (779), 8.58 (834), 8.40 (882). The ratio of the areas for dimer and monomer is roughly the ratio of the iron atoms per molecule. The constancy of the areas with changes in temperature is consistent with vibronic transitions.

Example spectra of $\mathrm{FeCl_3(g)}$ and $\mathrm{Fe_2Cl_6(g)}$ at 523 K are presented in the following paper.[7]

Vapor Pressure. In an earlier paper,[3] we reviewed the many nonspectral vapor pressure studies on solid iron(III) chloride and combined the results with those based on our observed absorbances at 360 nm to derive an overall vapor pressure–temperature equation for the equilibrium

$$2\mathrm{FeCl_3(s)} = \mathrm{Fe_2Cl_6(g)} \tag{7}$$

The spectrum of the dimer has an absorbance maximum at 360 nm. We have repeated the calculation using the molar absorptivities derived in the present work.

The vapor pressure–temperature equation may be written in the form

$$\ln\,[P\,(\mathrm{atm})] = 29.69(\ln T) - 0.06472T + (1.85 \times 10^{-5})T^2 - \Delta H^*/RT + \Delta S^*/R \tag{8}$$

which includes $\Delta C_P{}^\circ$ terms.[5] The least-squares $\Delta H^*/R$ and

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$\Delta S^*/R$ values are respectively 12 700 (±0.96%) and −135.99 (±0.07%) for the nonspectral data (77 observations) and 12 912 (±0.68%) and −135.49 (±0.14%) for the spectral data (49 values based on the new molar absorptivity equations at 360 nm). At 425, 500, and 575 K, the vapor pressures based on the nonspectral data are $(3.2 \pm 0.6) \times 10^{-5}$, $(9.9 \pm 1.5) \times 10^{-3}$, and 0.60 ± 0.07 atm, respectively. The corresponding pressures based on the spectral data with the new molar absorptivities are 3.2×10^{-5}, 1.1×10^{-2}, and 0.68 atm and with the previous molar absorptivities are 3.6×10^{-5}, 1.2×10^{-2}, and 0.76 atm. The match between the nonspectral and the spectral vapor pressures is now more reasonable with the new molar absorptivities. A least-squares treatment of the combined data (126 total observations) gives the recommended constants, 12 613 (±0.35%) and −136.15 (±0.07%). The combined-data equation covers a range of 425–575 K and at 500 K gives $\Delta H°$ and $\Delta S°$ values of 132 190 J/mol and 226.10 J/(K mol), respectively. These values correlate with those from a recent pressure study, within the reported large experimental uncertainty of ±7%.[13]

Supplementary Material Available: Table IV, experimental absorbances for the samples at the various wavelengths and temperatures (3 pages). Ordering information is given on any current masthead page.

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Iron(III) Chloride Hydrate in the Vapor Phase

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Spectrophotometric evidence indicates that iron(III) chloride hydrate vapor molecules are of major importance in certain $FeCl_3$–Cl_2–HCl–H_2O vapor mixtures. Molar absorptivities for the hydrate vapor molecule have been derived at 10-nm intervals over the wavelength range 240–440 nm in the temperature range 415–640 K. Values for the standard enthalpy of formation, −590 kJ mol^{-1}, and the standard entropy, 471 J mol^{-1} K^{-1}, for $Fe(H_2O)Cl_3(g)$ at 500 K are derived from equilibrium data. Between 415 and 475 K, the variation of the vapor absorbance with the concentration of water vapor indicates that a condensed hydrate phase with empirical composition $Fe_2Cl_6(H_2O)_3$ is present.

Introduction

In an earlier investigation of the vapor phase generated by heating hydrogen chloride and iron(III) oxide mixtures, evidence was found for the presence of iron(III) chloride hydrate, $Fe(H_2O)Cl_3$, molecules.[1] We now report an extended spectrophotometric study of the $FeCl_3$–Cl_2–HCl–H_2O system. Vapor-phase absorbances of homogeneous mixtures with different compositions may be explained by assuming that the dominant equilibrium at temperatures below 600 K is

$$0.5Fe_2Cl_6(g) + H_2O(g) = Fe(H_2O)Cl_3(g) \qquad (1)$$

Molar absorptivities at wavelengths over the range 240–440 nm (10-nm intervals) and thermodynamic constants are derived for the gaseous hydrate molecule.

Experimental Section

The reactants (see Table I) were introduced, under vacuum, into cylindrical quartz absorption cells of 5 cm path length and 1.9 cm i.d. A quartz tube (ca. 20 cm long with 2 and 4 mm o.d. sections) was attached at the center of each cell. A small piece of iron wire (Baker and Adamson standardization wire, 99.90%) was inserted into this side arm, which was then connected to the Pyrex vacuum system by using a graded quartz–Pyrex seal. The system was evacuated. Chlorine was generated by thermal decomposition of anhydrous copper(II) chloride. The gas was liquefied, and then small amounts were vaporized (from an excess of liquid) into the cells. The mixtures were flamed lightly to form iron(III) chloride and desired amounts sublimed into the cells. Small excesses of chlorine, sufficient to prevent decomposition of iron(III) chloride into solid iron(II) chloride, and known amounts of dry hydrogen chloride (Matheson) were then condensed into the cells with use of liquid nitrogen.

Hydrogen chloride was added to prevent the interaction of water and iron(III) chloride to form iron(III) oxide and/or iron(III) oxychloride. The samples of hydrogen chloride were vaporized from an excess of condensed liquid. Amounts were calculated with use of measured pressures in calibrated volumes and the perfect-gas law. The gas passed through a dry-ice trap before it entered the cell. The mixture in each cell was then isolated by collapsing a section of the side arm.

Table I. Initial Reactant Concentrations (mol L^{-1})

sample no.	$10^6C_{FeCl_3}$[a]	$10^4C_{H_2O}$[b]	10^2C_{HCl}[b]	$10^4C_{Cl_2}$[b]
1	26.8 ± 0.5	39.7	2.56	1.0
2	9.9 ± 0.4	38.5	2.63	3.0
3	24.3 ± 0.6	(12.5)[d]	2.50	2.3
4	16.8 ± 0.3[c]	(6.90)[d]	1.02	1.0
5	8.9 ± 0.1	39.1	2.66	2.1
6	50.0 ± 1.0	15.0	2.66	2.2
7	28.1 ± 0.5	19.4	2.38	0.8
8	53.2 ± 0.9	8.59	2.58	4.4

[a] Based on an analytical determination of iron; ± values are estimated uncertainties. [b] Estimated uncertainty: H_2O, 2%; HCl, 1%; Cl_2, 5%. [c] 16.2 ± 0.3 calculated from the absorbance at 360 nm before addition of water. [d] Adjusted; see Results and Discussion.

Chlorine concentrations were determined from measured absorbances at 330 nm at room temperature; at higher temperatures the absorbances of iron(III) chloride vapors were measured at 360 nm to see that the desired amounts were present.[2] The calculated spectral concentrations of iron agreed with those found by analysis except for sample 4 (see Table I). Absorbances were measured with a Cary 14H spectrophotometer.

The cells were then reconnected to the vacuum system and measured amounts of water introduced by one of two methods. For three samples a short piece of thick-walled Tygon tubing was used. The side arm of a sealed cell was scored with a file and slipped into the snug-fitting tubing that was connected to the vacuum system. After evacuation of the assembly, the tip was broken off by bending the tubing and then a measured amount of water vapor was condensed into the cell, cooled with liquid nitrogen.

In the second method, used for the other samples, a slightly larger section (4 mm o.d.) of the quartz side arm of a sealed cell was slipped into a tight-fitting tubular end of a Pyrex ball joint and sealed with black vacuum wax. The tip of the side arm (2 mm o.d.), scored with a file near the ball joint, extended through the joint into the matching half that was attached to the vacuum system. After evacuation of the assembly, the tip was broken off by tilting the halves of the joint slightly. A measured quantity of water vapor was then condensed into the cell, cooled with liquid nitrogen.

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(2) Rustad, D. S.; Gregory, N. W. *Inorg. Chem.*, preceding paper in this issue.

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