where, in a typical reaction, 0.346 g (1.47 mmol) of P_4O_7 was transferred into the apparatus. The vessel containing the P_4O_7 was sealed with a stopcock adapter, removed from the drybox, and attached to a vacuum line. Approximately 3 mL of toluene was vapor transferred into the reaction vessel. The solution (ca. 0.49 M in P_4O_7) was frozen at −196 °C, and 1.0 mmol of $Ni(CO)_4$ was condensed into the vessel. The temperature was slowly raised to 0 °C, with concomitant CO evolution. The reaction temperature was maintained at 0 °C for 1.5 h, and then was quenched at −196 °C. The vessel was reevacuated, allowed to warm to −78 °C to degas and again cooled to −196 °C, and reevacuated. The solution was warmed to −78 °C and was then poured into an attached NMR tube that had been precooled to −78 °C. Sufficient solution was poured into the cooled NMR tube to reach a depth of ca. 3 cm. The tube and bulk solution were frozen at −196 °C, and the NMR tube was flame sealed, removed from the reaction vessel, and stored at −196 °C. A ^{31}P NMR spectrum showed a mixture of products, with $[Ni(CO)_3](P_4O_7)$ dominating. The entire process was repeated with the addition of a second millimole of $Ni(CO)_4$ with 1.5 h of reaction at 0 °C. The second NMR tube contained as the primary component $[Ni(CO)_3]_2(P_4O_7)$. Upon addition of a third millimole of $Ni(CO)_4$ and repeating the above process, the ^{31}P NMR spectrum indicated that $[Ni(CO)_3]_3(P_4O_7)$ was the major product. All ^{31}P NMR spectra were recorded at −16 °C to prevent product decomposition with subsequent evolution of CO.

$[Fe(CO)_4]_n(P_4O_7)$, n = 1, 2. The reaction between $Fe_2(CO)_9$ and P_4O_7 was carried out in a drybox. To 50 mL of dry glyme was added 1.0 g (2.8 mmol) of $Fe_2(CO)_9$, and 0.7 g (2.9 mmol) of P_4O_7. The mixture was vigorously stirred magnetically for 3 h at 40 °C. A 5-mL aliquot of the solution was removed and the solvent evaporated from it. To the remaining green residue was added 1.0 mL of dry degassed benzene. The major product, as shown by ^{31}P NMR, was $[Fe(CO)_4](P_4O_7)$. To the remaining glyme solution was added another 1.0 g of $Fe_2(CO)_9$, and the solution was stirred for 3 h. After being cooled, the reaction mixture was treated as above; the ^{31}P spectrum showed $[Fe(CO)_4]_2(P_4O_7)$ to be the major product.

$[M(CO)_5](P_4O_7)$, M = Cr, Mo, W. Into a 50-mL, three-necked round-bottom flask was added under inert atmosphere 20 mL of dry THF, 0.53 g (2.26 mmol) of P_4O_7, and 0.80 g (3.6 mmol) of $Cr(CO)_6$. The solution was stirred until dissolution of the carbonyl and was UV irradiated from the underside of the flask for 2 h. Irradiation was ceased, and the solvent was removed by vapor transfer. The flask was transferred into the drybox, and the residue was treated with 2 mL of dry benzene. The ^{31}P NMR of the benzene solution showed $[Cr(CO)_5](P_4O_7)$. For the preparation of the molybdenum analogue, the above procedure was used with 0.30 g (1.30 mmol) of P_4O_7 and 0.50 g (1.90 mmol) of $Mo(CO)_6$ with 2.5 h of irradiation. The tungsten analogue was prepared using 1.30 mmol of $W(CO)_6$ and 0.90 mmol of P_4O_7, with 3.5 h of irradiation. The reaction of $Mo(CO)_6$ produced some disubstituted product $[Mo(CO)_5]_2(P_4O_7)$, in addition to the monosubstituted product.

Tensimetric Titrations. In a drybox a known quantity (typically 0.1–0.2 mmol) of P_4O_7 was placed in a tensimeter.[14] The tensimeter was transferred to a vacuum line, and ca. 3.0 mL of dry toluene was vapor transferred onto the P_4O_7. The particular Lewis acid (BF_3, BMe_3, and B_2H_6) was then vapor transferred into the tensimeter in increments corresponding to ca. 1:4 mole ratio of the P_4O_7 used. After each addition the solution was rapidly stirred and maintained at −78 °C for 1.5–2 h, to ensure equilibrium conditions, before a pressure reading was taken.

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Registry No. $[Ni(CO)_3](P_4O_7)$, 64045-11-0; $[Ni(CO)_3]_2(P_4O_7)$, 64045-10-9; $[Ni(CO_3)]_3(P_4O_7)$, 64045-09-6; $[Fe(CO)_4](P_4O_7)$, 64045-08-5; $[Fe(CO)_4]_2(P_4O_7)$, 64045-07-4; $[Cr(CO)_5](P_4O_7)$, 64045-06-3; $[Mo(CO)_5](P_4O_7)$, 64045-05-2; $[Mo(CO)_5]_2(P_4O_7)$, 64045-04-1; $[W(CO)_5](P_4O_7)$, 64070-32-2; $(BF_3)_2(P_4O_7)$, 64056-83-3; $Ni(CO)_4$, 13463-39-3; $Fe_2(CO)_9$, 15321-51-4; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

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Gas-Phase Ultraviolet and Visible Spectra of Sodium Tetrachloroferrate(III) and of Monomeric and Dimeric Iron(III) Chloride

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Molar absorptivities in the ultraviolet and visible range for $FeCl_3(g)$ at 400–650 °C, $Fe_2Cl_6(g)$ at 200–600 °C, and $NaFeCl_4(g)$ at 450–650 °C have been evaluated; the temperature dependence of the vaporization of $NaFeCl_4$ from a liquid phase in equilibrium with NaCl(s) has also been studied spectrophotometrically. The vapor-phase spectra of these molecules, along with $FeAlCl_6$, are discussed in terms of the different chlorine environments of the iron atoms and are compared with condensed-phase spectra of similar species as reported by other authors.

Introduction

A previous spectrophotometric study[1] of gaseous Fe_2Cl_6 and $FeAlCl_6$ has shown these substances to have similar charge-transfer ultraviolet and visible spectra with absorption maxima at 245 and 360 nm. Molar absorptivities of $FeAlCl_6$ are lower, by about one-third at 245 nm and by about one-half at 360 nm, than those of Fe_2Cl_6. The two molecules are expected to have similar structures (fourfold chlorine coordinated metal atoms joined by sharing two of the chlorine

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atoms, a double chlorine bridge) and the lower absorptivities for the mixed-metal dimer was related to the reduced number of iron–chlorine bonds.

In the solid phase sodium tetrachloroferrate(III) has essentially an ionic structure, $Na^+(FeCl_4^-)$. Fe–Cl bond distances are not substantially different for bridging chlorine atoms (those between the sodium atoms and the iron atoms) and nonbridging chlorine atoms.[2] Iron atoms have a slightly distorted tetrahedral environment of chlorine atoms. In various solvents the $FeCl_4^-$ ion is also apparently tetrahedral and shows three main charge-transfer absorption maxima, at 240–242, 312–317, and 360–364 nm.[3-6] Transpiration experiments indicate that gaseous $NaFeCl_4$ is predominantly monomeric.[7] The iron atoms in $FeCl_3$ assume various coordination environments in different solvent systems; spectral behavior varies considerably around 200–300 nm but is quite consistent in the 350–360-nm region.[5,6,9] Octahedral coordination is found in crystalline $FeCl_3$.[8] The monomeric vapor molecule has only three iron–chlorine bonds; a rough estimate of its spectra has been reported previously by Shieh and Gregory.[1]

In the present work the ultraviolet and visible spectra of $NaFeCl_4$(g), $FeCl_3$(g), and Fe_2Cl_6(g) have been measured in the temperature range 400–650 °C and, along with the spectra reported earlier for $FeAlCl_6$(g), are discussed relative to the different chlorine environments of the iron atoms. Gas-phase spectra are compared with those observed by other investigators for similar compounds in solutions.

Experimental Section

The procedures for the preparation of iron(III) chloride samples in quartz cells and the instrumentation for heating and recording the spectra were basically the same as described previously.[1] Cells were sealed off on the quartz side of the quartz–Pyrex graded seals to permit study of these systems at higher temperatures. The amounts of iron in the cells were determined by atomic absorption spectroscopy (Perkin-Elmer, Model 303). Standard solutions for calibration were prepared from standard iron wire (Allied Chemical) and nitric acid.

To prepare samples of $NaFeCl_4$, excess amounts (0.2–0.5 mg) of finely powdered sodium chloride (Mallinckrodt, Analytical Reagent) were first placed in the cells. The cells were then evacuated and heated with a flame to drive off traces of moisture. Subsequently, iron(III) chloride was prepared and sublimed (in vacuo) into each cell, and the resulting mixture heated to produce $NaFeCl_4$.[7]

Results and Discussion

Monomeric and Dimeric Iron(III) Chloride. Thermodynamic data relating to the equilibrium

$$Fe_2Cl_6(g) \overset{K_1}{\rightleftharpoons} 2FeCl_3(g) \qquad (1)$$

have been reviewed and tabulated in the JANAF tables.[10] Molar absorptivities for the monomer and the dimer were derived from the relationships

$$C_{Fe} = C_M + 2C_D \qquad (2)$$

$$K_1 = C_M{}^2/C_D \qquad (3)$$

$$A/b = \epsilon_M C_M + \epsilon_d C_D \qquad (4)$$

C_{Fe}, C_M, and C_D, respectively, represent concentrations (mol/L) corresponding to the total amount of Fe, actual amount of monomer (M), and actual amount of dimer (D) in the cell. 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, respectively. Results are shown in Table I (200–480 nm; absorbances were negligible between 500 and 700 nm). The predicted degree of dissociation of the dimer is very small in the range 200–300 °C and ϵ_D values were calculated directly from C_{Fe} in this interval. For the range of C_{Fe} values used, the variation of C_D/C_M and its magnitude were such as to give reasonable precision for the molar absorptivities of monomeric $FeCl_3$ vapor only between 400 and 650 °C. In this interval the apparent variations of ϵ_M and ϵ_D with temperature were within experimental error and a least-squares treatment based on eq 4 was used to derive mean values of these constants. Values of b, C_{Fe}, and the concentration of Cl_2[11] for each of the four samples studied were: 10.0, 0.748×10^{-5}, 0.33×10^{-4}; 10.0, 0.963×10^{-5},[12] 0.74×10^{-4}; 5.00, 4.88×10^{-5}, 2.21×10^{-4};[13] 5.00, 6.65×10^{-5}, 9.04×10^{-4}; [13]

Table I. Molar Absorptivities[a] (L mol^{-1} cm^{-1}) for Fe_2Cl_6(g) and $FeCl_3$(g)

	$\epsilon_{Fe_2Cl_6(g)} \times 10^{-3}$				$\epsilon_{FeCl_3(g)} \times 10^{-3}$
λ, nm	200 °C	250 °C	300 °C	400–600 °C	400–650 °C
200	2.94	2.83	3.3 ± 0.2	3.3 ± 0.2	4.7 ± 0.2
210	3.85	3.70	4.0 ± 0.1	4.5 ± 0.2	3.7 ± 0.2
220	6.0	5.8	6.0	6.7 ± 0.2	2.3 ± 0.2
230	8.2	8.0	8.1	8.3 ± 0.2	1.6 ± 0.2
240	10.5	10.1	10.0	9.7 ± 0.2	2.1 ± 0.2
245	10.8	10.6	10.4	10.2 ± 0.2	
250	10.6	10.4	10.4	10.2 ± 0.2	3.2 ± 0.2
260	9.4	9.4	9.6	9.4 ± 0.2	4.0 ± 0.2
270	8.3	8.3	8.6	8.7 ± 0.2	3.6 ± 0.2
280	7.3	7.4	7.7	7.8 ± 0.1	3.0 ± 0.1
290	6.3	6.3	6.6	6.8 ± 0.1	2.7 ± 0.1
300	5.1	5.3	5.4	5.9 ± 0.1	2.7 ± 0.1
310	4.6	4.7	4.9	5.3 ± 0.1	3.3 ± 0.1
320	4.8	4.7	5.0	5.5 ± 0.1	4.1 ± 0.1
330	5.7	5.7	5.9	6.3 ± 0.1	5.1 ± 0.1
340	7.6	7.4	7.4	7.5 ± 0.1	5.8 ± 0.1
350	9.8	9.3	9.1	8.9 ± 0.1	6.0 ± 0.1
360	10.7	10.3	10.0	9.6 ± 0.1	5.8 ± 0.1
370	10.3	10.0	9.8	9.4 ± 0.1	5.3 ± 0.1
380	8.6	8.6	8.6	8.7 ± 0.1	4.6 ± 0.1
400	5.1	5.3	5.5	6.0 ± 0.1	3.2 ± 0.1
420	2.67	2.93	3.19	3.8 ± 0.1	1.9 ± 0.2
440	1.42	1.62	1.77	2.3 ± 0.1	0.9 ± 0.2
480	0.50	0.63	0.69	1.3 ± 0.1	0.2 ± 0.2

[a] Unless otherwise indicated, the relative average deviation is 1–2%.

Table II. Molar Absorptivities[a] (L mol^{-1} cm^{-1}) for $NaFeCl_4$(g) (450–650 °C)

λ, nm	$10^{-3}\epsilon$	λ, nm	$10^{-3}\epsilon$	λ, nm	$10^{-3}\epsilon$
200	3.0 ± 0.8	280	3.5 ± 0.3	360	2.5 ± 0.2
210	2.2 ± 0.3	290	3.0 ± 0.2	370	2.3 ± 0.2
220	2.8 ± 0.3	300	2.8 ± 0.1	380	2.2 ± 0.2
230	3.6 ± 0.3	310	2.7 ± 0.1	400	1.6 ± 0.1
240	4.2 ± 0.3	320	2.6 ± 0.1	420	1.2 ± 0.1
250	4.4 ± 0.2	330	2.6 ± 0.2	440	0.7 ± 0.1
260	4.2 ± 0.2	340	2.7 ± 0.1	480	0.4 ± 0.2
270	3.9 ± 0.2	350	2.6 ± 0.2		

[a] With average deviation.

Sodium Tetrachloroferrate(III). The equilibrium controlling the vapor concentration of $NaFeCl_4$ may be written

$$NaCl(s) + FeCl_3(g) \overset{K_2}{\rightleftharpoons} NaFeCl_4(g) \qquad (5)$$

and, in addition to eq 1 and 3, relationships (6)–(8) were used

$$C_{Fe} = C_M + 2C_D + C_C \qquad (6)$$

$$K_2 = C_C/C_M \qquad (7)$$

$$A/b = \epsilon_M C_M + \epsilon_D C_D + \epsilon_C C_C \qquad (8)$$

to derive molar absorptivities for $NaFeCl_4$(g), where C_C and ϵ_C are the concentration (M) and molar absorptivity of $NaFeCl_4$(g), respectively. Values of the equilibrium constant K_2 were taken from Richards and Gregory;[7] their results (measured in the range 350–530 °C) were extrapolated to predict values up to 650 °C. Equations 3, 6, and 7 were used to find the concentration of each species, which together with eq 8 and the molar absorptivities of the monomer and dimer,

Table III. Data for $NaFeCl_4$ Samples (Path Lengths $b = 5.00$ cm)[a]

	Sample 1; $C_{Fe} = 5.47 \times 10^{-5}$ M, $C_{Cl_2} = 3.60 \times 10^{-5}$ M						
T, °C	650 ± 3	598 ± 2	580 ± 2	562 ± 3	552 ± 2	540 ± 2	530 ± 2
$A(250)$	1.067	1.105	1.137	1.120	0.980	0.853	0.740
$A(350)$	0.945	1.016	1.105	1.000	0.897	0.772	0.672
	Sample 2; $C_{Fe} = 2.35 \times 10^{-5}$ M, $C_{Cl_2} = 0.0$						
T, °C	602 ± 6	544 ± 4	519 ± 5	476 (neck) 523 ± 10	411 (neck) 522 ± 15		
$A(250)$	0.495	0.505	0.445				
$A(350)$	0.427	0.440	0.403	0.260	0.110		
	Sample 3; $C_{Fe} = 1.05 \times 10^{-5}$ M, $C_{Cl_2} = 5.00 \times 10^{-5}$ M						
T, °C	599 ± 1	550 ± 2	500 ± 1	451 ± 1	426 ± 2	399 ± 1	
$A(250)$	0.224	0.224	0.217	0.217			
$A(350)$	0.186	0.186	0.187	0.187	0.167	0.117	

[a] Unless otherwise indicated, temperatures represent the average of those measured at neck tip, center, and cell window,[1] with the average deviation from the mean given. For sample 2 the neck temperature was used in *plotting the vapor pressures* (Figure 1).

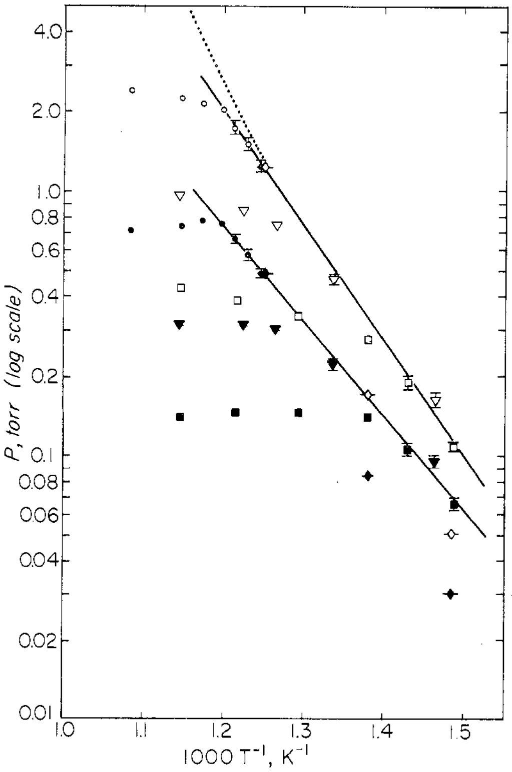


Figure 1. Partial pressures of $FeCl_3$ and $NaFeCl_4$ in equilibrium with NaCl(s) and, at lower temperatures, with a liquid phase saturated with NaCl(s). Open symbols represent values for $NaFeCl_4$ and filled symbols values for $FeCl_3$. See Table III. Samples 1, 2, 3 are designated by ○, ▽, □; ref 7, -◇-; ref 15, ···. Error bars on saturated vapor pressures are average deviations based on spectral data.

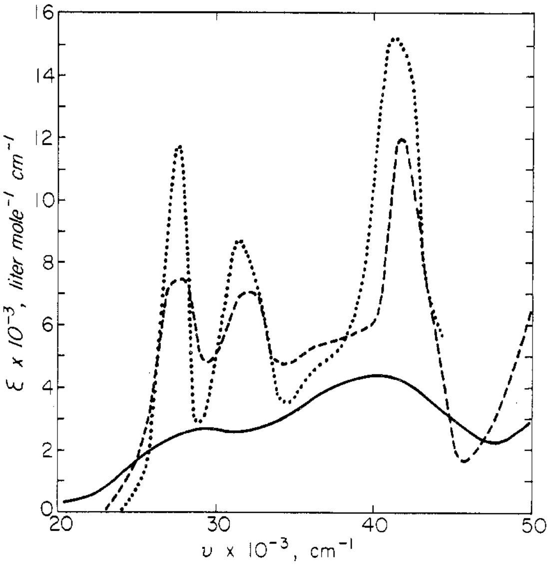


Figure 2. Ultraviolet and visible spectra for tetrachloroferrate (III) compounds: —, $NaFeCl_4(g)$ in range 450–650 °C (Table II); - - -, average molar absorptivities for $MFeCl_4$ ($M^+ = Li^+, K^+, H^+$) in various solvents at room temperatures;[4-6] ···, $(n\text{-}C_4H_9)_4NFeCl_4$ in ethanolic glass at 77 K.[3]

lead to the values of ϵ_C listed in Table II.

The amounts of iron and of excess chlorine for each of the three samples are indicated in Table III. No chlorine was added to the second sample; at the temperatures used the decomposition of ferric to ferrous chloride was assumed negligible.[7,14] The concentration of iron in the second sample was determined by comparison with a Beer's law plot of the absorbances of the other samples at 600 °C where the concentration of $Fe_2Cl_6(g)$ is negligible; in this case

$$C_{Fe} = (A/b)(1 + K_2)/(\epsilon_M + K_2\epsilon_C) \qquad (9)$$

At lower temperatures, Figure 1, it was necessary to increase the temperature gradient between the cell windows and the cell neck to avoid condensation of a liquid complex phase on the windows. However, in all but two experiments (see Table III), cell body, neck and window temperatures were within 6 °C or less. Partial pressures derived for $FeCl_3$ and for $NaFeCl_4$ are shown in Figure 1. When all of the iron was in the vapor phase, partial pressures were calculated using eq 3, 6, and 7. As the temperature decreases, the fraction of Fe_2Cl_6 becomes increasingly important. Also, K_2 increases with increasing temperature so the partial pressures of $NaFeCl_4$ and $FeCl_3$ diverge. When a condensed phase containing iron was present, eq 3, 7, and 8 together with the molar absorptivities were used to derive the partial pressures. An excess of solid sodium chloride was present at all temperatures in all of the samples. After cooling of the samples to room temperature yellow $(NaFeCl_4)$[7,16] and white (NaCl) solids were observed.

Equations 3, 6, 7, and 8 may be combined in a way which suggests that values of K_2 and ϵ_C can be obtained only by use of the measured absorbances and the total concentration of iron. However, this approach was found not to be practical. It requires that Fe_2Cl_6 make a significant contribution to the absorbance when all the iron is in the vapor phase and this could not be realized in a range where the absorbances could be measured with good accuracy.

Spectra. Spectra reported for various tetrachloroferrate(III) compounds are reproduced in Figure 2 along with that for $NaFeCl_4(g)$. In ref 3 a 77 K spectrum of $FeCl_4^-$ in an ethanolic glass was given only with "arbitrary" absorbance units. To produce a spectrum comparable to that of the present work, the given observed oscillator strengths based on Gaussian curves and the measured peak widths at half the absorption maximum were used to calculate peak ϵ_{max} values[4]

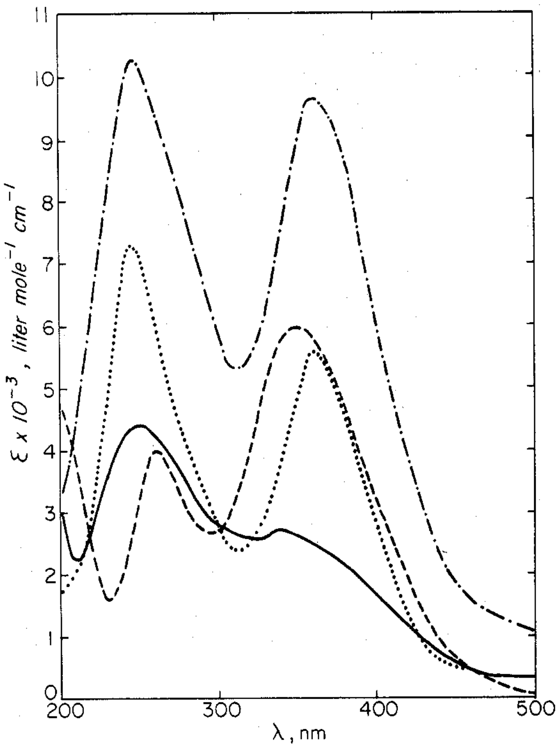


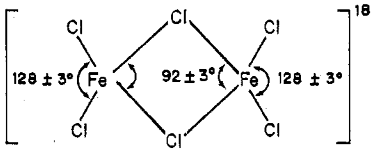
Figure 3. Ultraviolet and visible spectra for $NaFeCl_4$ (—, 450–650 °C), $FeCl_3(g)$ (---, 400–650 °C), $Fe_2Cl_6(g)$ (-·-·, 400–600 °C), and $FeAlCl_6(g)$ (···, 200 °C).

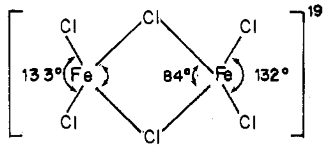
from which the other spectral values could be calculated on a relative basis. As compared with the solid at 77 K, the vapor at 450 °C shows a marked decrease in molar absorptivities and broadening of the peaks. Between 450 and 650 °C the change of ϵ_C with temperature lies within experimental scatter (a similar behavior was observed for Fe_2Cl_6 (see Table I)); a slight reduction in ϵ_D with increasing temperature between 200 and 400 °C was noted. In view of the loss of features in the high-temperature $NaFeCl_4$ spectrum, resolution into Gaussian curves was not attempted. However, the ratios of the maximum molar absorptivities at (40–42) × 10^3 cm^{-1} to the averages at (27–32) × 10^3 cm^{-1} are very similar (1.6 ± 0.1) for all the $FeCl_4^-$ spectra. This suggests, within the sensitivity of ultraviolet and visible charge-transfer spectra to structural changes (see below), that the chlorine environments of the iron are similar in the gaseous phase and in the solutions. In the latter the accompanying cation appears to have no major influence. $NaFeCl_4(g)$ is presumably best described as molecular (albeit with considerable ionic character for the sodium atom); ions or ion pairs may be expected in the solutions with the molecular form dominating for the weak acid $HFeCl_4$.[5]

Bird and Day[3] associated the peaks shown by $FeCl_4^-$ at 77 K at 364 nm (2.75 μm^{-1}), 317 nm (3.152 μm^{-1}), 270 nm (3.70 μm^{-1}) and 242 nm (4.125 μm^{-1}) with electronic transitions identified as $t_1 \rightarrow 2e$, $t_1 \rightarrow 4t_2$, $3t_2 \rightarrow 2e$, and $3t_2 \rightarrow 4t_2$, respectively. t_1 and $3t_2$ are described as states for which the major contributions come from nonbonding and π-bonding orbitals of the ligand, respectively, and 2e and $4t_2$ as states having largely the character of the metal 3d orbitals. If this assignment is applicable to the high-temperature spectrum of $NaFeCl_4$, it would appear that the first two transitions are unresolved in the peak around 340 nm and the second two are unresolved in the peak around 250 nm.

The general similarities in the spectra of $NaFeCl_4$, $FeCl_3$, Fe_2Cl_6, and $FeAlCl_6$, compared in Figure 3, suggest that similar transitions occur in these molecules. (It should be noted in the comparison that the spectrum shown for $FeAlCl_6$ was taken around 200 °C; a decrease of ϵ_{max} of about 10% and a slight broadening of the peaks are to be expected for a spectrum at 400–600 °C, the temperature range for the other compounds.) Only small shifts are observed in the wavelengths of the peak maxima. However, significant differences are noted in the ϵ_{max} values. The question of the relative intensities to be expected for corresponding transitions in these molecules is a complex matter. However, qualitatively, we note that in addition to a difference related to the number of iron atoms in the dimer molecules the peak heights also seem related to certain aspects of the molecular geometry.

The bond angles reported for Fe_2Cl_6 are significantly distorted from those expected for two shared regular tetrahedra.[18,19]





The bridge angles reported for Al_2Cl_6 are somewhat larger (101 ± 10°) and the terminal bond angles smaller (118 ± 6°).[20] The ratio of the spectral area under the peaks for Fe_2Cl_6 to that for $FeAlCl_6$ is 2/1, the same as is the ratio of the numbers of iron atoms in the molecules. The absorbance around 240 nm is relatively enhanced compared to that near 360 nm when Fe–Cl bond angles are closer to tetrahedral values, as in $NaFeCl_4$, but the reverse is observed for larger bond angles as in trigonal-planar $FeCl_3$. Interestingly Fe_2Cl_6 and $FeAlCl_6$, with characteristics of both geometries, absorb relatively strongly in both regions. The higher $\epsilon_{245}/\epsilon_{360}$ ratio for $FeAlCl_6$ would imply, on this basis, that the chlorine environment around the iron atom in this molecule is closer to tetrahedral than that in Fe_2Cl_6, as expected on comparison of the structures of Al_2Cl_6 and Fe_2Cl_6.

Partial Pressures in the Presence of a Liquid Sodium Tetrachloroferrate(III) Phase. Cook and Dunn[15] (see Figure 1) have reported equilibrium vapor pressures expected for pure liquid $NaFeCl_4$. Pressures were calculated, using Raoult's law, from the results of transpiration experiments in which Cl_2 gas was bubbled through melts of nominal NaCl mole fractions of 0.514–0.650 in the temperature interval 480–830 °C. The phase diagram for the NaCl–$FeCl_3$ system[15] indicates that the composition of the liquid solution saturated with NaCl(s) stays near that corresponding to $NaFeCl_4$, changing only from $X_{NaCl} \approx 0.51$ to 0.55, over the temperature range 160–530 °C. Richards and Gregory[7] also used transpiration experiments (350–530 °C) with argon and chlorine as the primary carrier gas, flowing first over $FeCl_3(s)$, at lower temperatures, and then over NaCl(s), with a substantial excess of the latter present. In their work $FeCl_3$ partial pressures were varied over a wide range to test the constancy of the ratio $NaFeCl_4$:$FeCl_3$, predicted for reaction 5. In two of their experiments (at 530 °C) the equilibrium vapor was generated without prior introduction of $FeCl_3$ into the carrier gas, which flowed over a liquid sodium tetrachloroferrate(III) phase saturated with NaCl(s). The values of P_{NaFeCl_4} and P_{FeCl_3} derived from these experiments are seen (Figure 1) to agree well with those of Cook and Dunn and those derived in the present work. At lower temperature their[7] partial pressures are below those found in our study, as would be expected if their partial pressures of $FeCl_3$ were insufficient to form the saturated liquid phase. Measurement of the equilibrium constant for (5) does not, of course, require the presence of the liquid phase.

Our results shown in Figure 1 converge with those of ref 7 and 15 at higher temperatures but diverge at lower temperatures and lead to the following apparent enthalpies and entropies of vaporization.

$$\text{NaFeCl}_4\ (\text{liq, satd with NaCl(s)}) = \text{NaFeCl}_4(\text{g})$$

$$\Delta H^\circ = 19.9\ \text{kcal mol}^{-1};\ \Delta S^\circ = 12.1\ \text{cal deg}^{-1}\ \text{mol}^{-1}$$

$$\text{NaFeCl}_4\ (\text{liq, satd with NaCl(s)}) = \text{FeCl}_3(\text{g}) + \text{NaCl(s)}$$

$$\Delta H^\circ = 16.6\ \text{kcal mol}^{-1};\ \Delta S^\circ = 6.2\ \text{cal deg}^{-1}\ \text{mol}^{-1}$$

The values for $NaFeCl_4$ are appreciably less than those based on the data of Cook and Dunn (27.5 kcal and 21.6 cal mol^{-1} deg^{-1}). The effect of the different compositions of the liquid phase must be considered, and in our case, the amount of material in the liquid phase is very small; i.e., the liquid droplets at the point of initial condensation must be extremely small, and surface effects may have a substantial influence.

In a fourth study[21] vapor pressures derived from amounts of condensates produced in a temperature-gradient, static sealed-tube system appear much higher than the results shown in Figure 1.

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Registry No. $FeCl_3$, 7705-08-0; Fe_2Cl_6, 16480-60-7; $NaFeCl_4$, 15007-28-0; $FeAlCl_6$, 57606-43-6.

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(12) Determined from a Beer's law plot of the absorbances of the other three samples at 200 °C.
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The Acid–Base Chemistry of Oxide and Chalcogenide Ions in Sodium Tetrachloroaluminate Melts at 175 °C

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The acid–base chemistry of oxide, sulfide, selenide, and telluride ions in sodium tetrachloroaluminate melts at 175 °C has been investigated. These ions were found to be trichloro bases in acidic melts, the equilibrium with the solvent being $3Al_2Cl_7^- + X^{2-} \rightleftarrows AlXCl + 5AlCl_4^-$, where X^{2-} is the oxide or chalcogenide ion. In basic melts these ions become dibases, the equilibrium being $2Al_2Cl_7^- + X^{2-} \rightleftarrows AlXCl_2^- + 3AlCl_4^-$. Within the precision of the present results the relative strengths of the tribases appear to be in the order Te^{2-}, $Se^{2-} < S^{2-} < O^{2-}$.

Molten tetrachloroaluminates ($AlCl_3$–alkali chloride mixtures) have in recent years been the subject of considerable experimental investigations, both as potential electrolytes in molten salt battery systems and also because of their interesting acid–base properties. A number of possible cathode systems for batteries have been investigated, including sulfur[1] and selenium,[1,2] while the use of oxygen has also been suggested. The electrochemistry of the above systems has been briefly studied, but very little is known about the chemistry involved, particularly concerning the interactions between basic oxide or chalcogenide ions and the acid moieties in the melt. These interactions might have considerable influence on the operation of any battery system based on these materials. The behavior of the oxide ion is also of considerable interest as it is liable to be present in all tetrachloroaluminate melts as an impurity (from traces of water).

In a previous paper from this laboratory, a study of the acidity dependence of the S_2/S^{2-} redox potential in $NaAlCl_4$ melts was reported.[3] From this it was suggested that an acid–base equilibrium existed between S^{2-} ions and the melt (eq 1). By considering the various equilibria that exist between the species in the melt,[4] equilibrium 1 can be rewritten as eq 2. The sulfide ion appears to be behaving as a trichloro base under these conditions. The presence of these equilibria was also used to explain the very high solubility of metal sulfides observed in acidic melts.

$$AlCl_4^- + S^{2-} \rightleftarrows AlSCl + 3Cl^- \qquad (1)$$

$$3Al_2Cl_7^- + S^{2-} \rightleftarrows AlSCl + 5AlCl_4^- \qquad (2)$$

Letisse and Tremillon have briefly investigated the chemistry of O^{2-} ions in $NaAlCl_4$ melts.[5] They titrated O^{2-} ions (introduced as barium hydroxide, which yields H^+ and O^{2-} ions on contact with the melt) with the melt and showed the oxide ion to be a strong trichloro base. They proposed equilibrium 3, where $Al_2OCl_5^-$ is the solvated form of AlOCl. This observation was, they stated, further supported by the fact that addition of water to the melt reduced its acidity; the oxide ion must therefore be more than a dibase (the water yields $2H^+ + O^{2-}$ on contact with the melt, and H^+ is a monochloro acid). In a more recent paper,[6] however, Tremillon et al. have proposed instead that equilibrium 4 exists, except in very acidic

$$2AlCl_4^- + O^{2-} \rightleftarrows Al_2OCl_5^- + 3Cl^- \qquad (3)$$

$$2AlCl_4^- + O^{2-} \rightleftarrows Al_2OCl_6^{2-} + 2Cl^- \qquad (4)$$