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Spectrophotometric Study of Iron(II) Chloride Vapor and of Iron(II) Chloride–Iron(III) Chloride Vapor Mixtures and the Interaction of Iron(II) Chloride with Quartz and Pyrex

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Molar absorptivites of $FeCl_2(g)$ at 211, 241, and 274 nm (3800 ± 300, 4700 ± 300, and 1900 ± 100 M^{-1} cm^{-1}, respectively) and the standard enthalpy change (46.8 ± 0.2 kcal mol^{-1}) for the process $FeCl_2(s) = FeCl_2(g)$ have been derived from spectrophotometric data. No direct evidence for significant contributions from Fe_2Cl_4 was seen in absorbance data for saturated vapors in the temperature range 473–632 °C. Quantitative treatment of results for the unsaturated vapor is complicated by reaction of $FeCl_2$ with quartz and Pyrex at temperatures above 400 °C. These reactions, the effect of hydrogen chloride on the saturated vapor absorbances of small samples of $FeCl_2$, and the behavior of $FeCl_2$–$FeCl_3$ mixtures are discussed.

As part of continuing work on thermodynamic and spectroscopic properties of molecular species in iron halide vapor systems[1] a spectrophotometric study has been made of the vapor phase of iron(II) chloride and of iron(II) chloride–iron(III) chloride mixtures. A saturated iron(II) chloride vapor spectrum (200–400 nm) has been published previously.[2] However, separate contributions of monomer and dimer were not considered at that time and calculated molar absorptivities vary greatly depending on which of the several reported vapor pressure equations for $FeCl_2$ is used.[3] The present work was undertaken to clarify these questions and includes a study of unsaturated iron(II) chloride vapor; iron(II) chloride–iron(III) chloride vapor mixtures were also examined for evidence concerning the presence of Fe_3Cl_8. However, side reactions with Pyrex and quartz occur and have an important effect on observed absorbances of the unsaturated vapors. The effect of side reactions is diminished by the addition of hydrogen chloride and by the use of all-quartz containers, but for small samples the presence of hydrogen chloride affects the absorbances of saturated iron(II) chloride vapors. These features limit the information that can be derived from spectrophotometric study of iron halide vapors in Pyrex and quartz or in all-quartz containers. The observed effects are described in some detail because of their possible general importance for similar transition-metal halide systems.

Experimental Section

General Procedures. Samples were prepared in Pyrex and quartz or all-quartz systems to which were attached various quartz absorption cells (1.9 cm i.d., 1–10 cm path lengths) and side arms holding solid reagents. Assemblies were initially connected to a Pyrex high-vacuum line via a U-tube cooled in liquid nitrogen and were dried by flame heating under high vacuum. Condensed samples were vacuum sublimed into side arms leading to absorption cells, and, when desired, gaseous reagents such as HCl were condensed into the cells before flame seal off of the quartz side arm. Depending on the situation different parts of the system were cooled with liquid nitrogen during seal off to minimize the amount of water (driven from the fused quartz) that might enter the cell. Spectra were taken with a Cary 14H spectrophotometer. Temperatures were measured with chromel–alumel thermocouples calibrated at the melting points of aluminum and zinc.[4] The temperatures of the cell body, T_1, and the cell windows, T_2, together were controlled (±1 °C) independently of the temperature of the tip of the side arm, T_3. When a condensed phase was present, T_3 was kept below T_2 to prevent condensation of sample on the windows. For the majority of the measurements the temperature differential was less than 10 °C; in a very few cases, when the problem was exacerbated in 10-cm cells, the differential was as large as 60 °C. Pressure equilibrium within the cells was assumed and the derived pressure at T_3, taken as the temperature of the solid phase condensed in the tip, used to evaluate equilibrium constants controlled by the condensed phase. The vapor-phase temperature, designated as T, was taken as T_1 (for samples in 10-cm cells) or an average of T_1 and T_2 (for 5-cm, or smaller, cells).

Elemental Determinations. After the absorbance measurements amounts of iron in unsaturated vapor samples were determined by atomic absorption (Perkin-Elmer Model 403, furnace attachment). For calibration standard solutions were prepared from standard iron wire (Allied Chemical, 99.9%) dissolved in nitric acid. The final concentration of HNO_3 was adjusted to 2 wt %. Cell samples were also dissolved in 2% HNO_3; in some cases the amounts of iron in the cell body and side arm were determined independently. Aliquots of some of the solutions were used to determine amounts of sodium present, with a Beckman DU flame photometer at 590 nm calibrated with standard solutions prepared from Mallinckrodt Analyzed Reagent NaCl.

Amounts of chlorine in the various cells, generated by decomposition of $FeCl_3$ to $FeCl_2$, were determined by one of two methods. (1) Chlorine does not recombine with $FeCl_2(s)$ at a significant rate at room temperature.[5] When feasible a direct measurement of the chlorine absorbance at 330 nm was made at room temperature. A Cary 219 spectrophotometer was used. The molar absorptivity of chlorine was taken as 67.5 M^{-1} cm^{-1}.[6] (2) In an indirect method the chlorine was first condensed in the cell side arm and sealed off; the capsule was subsequently broken under distilled water and *o*-tolidine dihydrochloride reagent solution[8] immediately added. Time-dependent Beer's law plots of the absorbance of these solutions at 435 nm were compared with those of standard samples of chlorine prepared by decomposition of $CuCl_2(s)$.[7] The standard chlorine samples were first isolated in Cary 14H cells and the amounts determined from the vapor absorbance at 330 nm.

Introduction of Gases. Hydrogen chloride (Matheson) was admitted from a Pyrex storage bulb attached to the vacuum line. The pressure was measured manometrically (<0.5 atm) in a calibrated volume and the number of moles calculated from the ideal-gas law. The liquid-nitrogen bath around the U-tube leading to the cell assembly was replaced with a dry ice bath to permit transfer of HCl, which was condensed in the absorption cell cooled with liquid nitrogen. In some cases the amounts of HCl in the cells were approximated from the room-temperature absorbance at 190 nm, measured with a Cary 219 spectrophotometer, and a molar absorptivity of 37 M^{-1} cm^{-1}.[9]

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(1) D. S. Rustad and N. W. Gregory, *Inorg. Chem.*, **16**, 3036 (1977).
(2) C. W. DeKock and D. M. Gruen, *J. Chem. Phys.*, **44**, 4387 (1966).
(3) "JANAF Thermochemical Tables", Thermal Laboratory, Dow Chemical Co., Midland, MI, supplements Dec 31, 1970, June 30, 1965, June 30, 1967, March 31, 1961, Sept 30, 1964, and March 31, 1977.
(4) W. F. Roeser and H. T. Wensel in "Temperature, Its Measurement and Control in Science and Industry", Vol. 1, American Institute of Physics, Reinhold, New York, 1941, p 284.
(5) D. S. Rustad and N. W. Gregory, *Inorg. Nucl. Chem.* Lett., **16**, 521 (1980).
(6) D. J. Seery and D. Britton, *J. Phys. Chem.*, **68**, 2263 (1964); G. Burns and R. G. W. Norrish, *Proc. R. Soc. London, Ser. A*, **271**, 289 (1963); G. E. Gibson and N. S. Bayliss, *Phys. Rev.*, **44**, 188 (1933).
(7) R. R. Hammer and N. W. Gregory, *J. Phys. Chem.*, **68**, 3229 (1964).
(8) "Standard Methods for the Examination of Water, Sewage and Industrial Wastes", 10th ed., American Public Health Association, Inc., New York, 1955, p 233.

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When water was added, it was measured and transferred in a similar manner before the introduction of HCl. Water pressures in the calibrated volume were kept less than 70% of the saturation vapor pressure. The liquid-nitrogen bath around the U-tube was replaced with an ice bath during the transfer of water.

Hydrogen gas (Matheson), when added, was the last gas to be introduced. After thorough flushing, a portion of the vacuum system was filled to a desired pressure directly from the tank. An isolated sample was permitted to enter the cell assembly via a stopcock through a liquid-nitrogen-cooled U-tube and the pressure measured manometrically. The quartz side arm of the cell was then sealed off. Since it was necessary during the transfer to keep HCl (and H_2O when present) condensed in the cell with liquid nitrogen, allowance was made for the different temperature in calculating the amount of hydrogen in the cell. Pressure equilibrium was assumed and the cooled portion kept small to minimize the uncertainty.

Iron(II) Chloride. In one method of preparation standard iron wire was placed in a side arm of a cell, heated, and allowed to react with chlorine vapor. Usually a mixture of $FeCl_2$ and $FeCl_3$ was formed, which was isolated with the excess iron wire and heated further to convert $FeCl_3$ to $FeCl_2$. Some of the $FeCl_2$ was vacuum sublimed into the quartz side arm of the cell, and the tip containing excess iron wire and residual $FeCl_2$ was sealed off. In a second method $FeCl_2 \cdot 4H_2O$ (Baker Chemical Co., Analyzed Reagent) was dehydrated and $FeCl_2$ sublimed from residual material directly into the cell side arm. With this method the various reactant gases could be conveniently introduced after sublimation of $FeCl_2$.

Iron(II) Chloride–Iron(III) Chloride Mixtures. The mixtures were prepared by thermal decomposition or by photoreduction[5] of iron(III) chloride. In the first method a sample of $FeCl_3$ in excess chlorine was prepared from iron wire and chlorine in a cell assembly. The absorbance of the fully vaporized iron(III) chloride was measured to determine the amount present. This was checked by an iron determination after studies were completed. The $FeCl_3$ was sublimed into the upper section of the side arm and the excess chlorine condensed in the tip with liquid nitrogen and removed. The remaining part of the tip was then immersed in liquid nitrogen close to the level of the $FeCl_3$ deposit and the $FeCl_3$ slowly sublimed away with use of a flame. A white deposit of $FeCl_2$ formed as part of the $FeCl_3$ decomposed during sublimation, and the chlorine released was trapped. When visual inspection indicated that enough $FeCl_2$ had formed, the isolated Cl_2 was sealed off. The amount of chlorine, determined by the indirect method, together with the total iron in the cell allowed determination of the amounts of $FeCl_2$ and $FeCl_3$ in the final mixture.

In the photoreduction method, $FeCl_3$ was again prepared in excess chlorine and the amount determined spectrophotometrically. After removal of excess chlorine the $FeCl_3$ vapor was photolyzed at 220 °C until sufficient decomposition had occurred. The cell was quenched in liquid nitrogen, and the amount of chlorine generated was measured by the direct method. The chlorine was then isolated in the tip and sealed off. The amounts of $FeCl_2$ and $FeCl_3$ remaining were then known.

Melting Points. Samples in small sealed Pyrex or quartz tubes were placed in a hole drilled in a large aluminum block. The block was heated, and melting was observed through suitable view holes. The melting temperature was taken as that indicated by a thermocouple attached to the outer surface of the tube at the location of the condensed sample.

Results and Discussion

Absorbances of Saturated Vapors of Iron(II) Chloride. The spectra observed in the range 200–400 nm had essentially the same shape as those reported in ref 2, with the major peak at 241 nm. If the dominant vaporization process is

$$FeCl_2(s) = FeCl_2(g) \tag{1}$$

a least-squares treatment, with the assumption of a linear relationship between ln (AT/b) and $1/T_3$, where A is the absorbance and b the cell path length, may be used to derive a value for $\Delta H°_1$. Absorbances of various samples in group A, Figure 1, at the peak maxima, 211, 241, and 274 nm, the minima, 225 and 267 nm, and points on two shoulders, 230 and 250 nm, were treated independently and gave the following values and standard deviations of $\Delta H°_1$: 44 ± 2 (211, 2, 7), 46 ± 2 (225, 2, 7), 45.0 ± 0.9 (230, 9, 28), 46.8 ± 0.2 (241, 12, 83) (considered the "best" value on the basis of the smallest standard deviation and largest number of observations), 47.2 ± 0.4 (250, 10, 31), 46.9 ± 0.8 (267, 10, 31), and 45.1 ± 0.7 (274, 10, 31) kcal mol^{-1}. The wavelength in nanometers, number of samples, and number of data points are indicated in parentheses in each case. A plot of log $(A_{241}T/b)$ vs. $1/T_3$ is shown in Figure 1 as points labeled group A; the least-squares equation was ln $(A_{241}T/b) = (-23\,550 \pm 100)T_3^{-1} + (31.1 \pm 0.1)$.

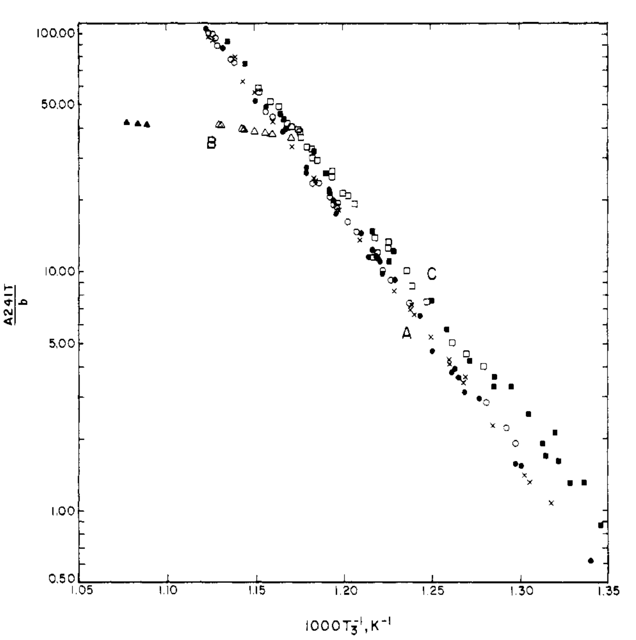

Figure 1. Temperature dependence of the absorbance at 241 nm of iron(II) chloride vapor under various conditions. Group A ($FeCl_2$ preparation): (●) prepared in Pyrex–quartz; (○) prepared in quartz; (×) prepared in quartz (relatively large amount with HCl added). Temperature range for the vapor was 830–951 K. Group B (sample prepared in Pyrex–quartz with HCl added, illustrating behavior above break-over point): (△) T_3 dependent; (▲) T dependent (plotted vs. $1000T^{-1}$ rather than T_3^{-1}). Group C (behavior of samples with relatively large concentrations of HCl and small amounts of $FeCl_2$): (□) prepared in Pyrex–quartz; (■) prepared in quartz. Temperature range for the vapor was 805–935 K.

JANAF thermodynamic constants[3] for reactions 1 and 2

$$2FeCl_2(g) = Fe_2Cl_4(g) \tag{2}$$

at our mean temperature of 850 K are 45.12 and −34.37 kcal mol^{-1} and 37.97 and −29.52 cal mol^{-1} deg^{-1} for $\Delta H°$ and $\Delta S°$, respectively. A least-squares treatment of the A_{241} data, based on the equation $A/bC_M = E_M + E_D(C_D/C_M)$, gave $E_M = 4520 \pm 50$ M^{-1} cm^{-1} and $E_D = 5400 \pm 1000$ M^{-1} cm^{-1}. C_M and C_D and E_M and E_D represent concentrations in mol L^{-1} and molar absorptivities of monomer and dimer, respectively. The maximum value of C_D/C_M predicted for our samples is only 0.13 (maximum contribution of dimer to absorbance 16%) with a large uncertainty reflecting uncertainty in the thermodynamic constants reported for the dimer.[3] An iteration in which $\Delta H°_1$ and $\Delta H°_2$ were permitted to vary so as to obtain the best least-squares fit led to the same result for $\Delta H°_1$ (46.8 kcal mol^{-1}) as the "best" value derived from the absorbance data when only the monomer was assumed present. We conclude that within the range and precision of our measurements the dimer does not have a concentration sufficiently high and/or a molar absorptivity sufficiently different from that of the monomer for absorbance data to give definitive evidence for its presence.

If the dimer is neglected and JANAF data[3] for (1) used, E_M values derived are 3800 ± 300 (at 211 nm), 4700 ± 300

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(9) J. Romand, *Ann. Phys. (Paris)*, [12] **4**, 529 (1949).

Table I. Unsaturated Iron(II) Chloride Vapor Samples Prepared in Quartz[a]

	10^5C_{Fe},[e] mol L^{-1}			10^5C_{Fe}, mol L^{-1}				
sample	cell body	side arm	10^5C_{HCl}	calcd[f]	condensed[g]	cell vol, cm^3	T, °C	$A_{241}/10C_{Fe(total)}$, 10^3 M^{-1} cm^{-1}
1[b]	1.37	0.11	nk	0.574	0.91	29.5	652	1.82
2[b]	3.53	nk	nk	2.39	1.14	30.6	655	3.18
3[b]	0.159	1.67	1.4[h]	0.813	1.02	30.4	624	2.09
4[b]	1.99	nk	10.6	1.30	0.69	28.2	655	3.07
5[c]	0.810	0.019	11.3	0.447	0.382	30.0	628	2.53
6[d]	1.43	0.002	64.9	1.17	0.26	30.7	653	3.83

[a] nk = not known; all in 10-cm cells. [b] Samples 1–4 held several hours or days at various temperatures as used to obtain saturation vapor absorbances. [c] At temperature for 1 h. [d] At temperature for 25 min. [e] Based on iron determination and cell volume. [f] Calculated as $A_{241}/10(4700)$. [g] Total $C_{Fe} - C_{Fe}$(calcd). [h] Produced from quartz reaction, measured spectrophotometrically; in samples 4–6, HCl was added. When the sample cooled, the vapor condensation occurred in the sidearm except for sample 3, where the vapor was condensed in the cell body.

(at 241 nm), and 1900 ± 100 (at 274 nm) M^{-1} cm^{-1}. Corresponding values reported in ref 2 are 5700, 7600, and 3000 M^{-1} cm^{-1}. The ratios 0.81:1.0:0.40 and 0.75:1.0:0.40, respectively, are in good agrement. The discrepancy in absolute values reflects a difference in the assumed vapor pressure; the JANAF values are based on a 1970 review of the work of a number of investigators.

When absorbances of vapors in equilibrium with $FeCl_2(s)$ were measured with HCl added to the system, five of the samples gave points falling in group C, Figure 1. Group A data were obtained from a variety of samples, prepared in Pyrex as well as quartz, with amounts of $FeCl_2$ varying from concentration equivalents of 9×10^{-6} to 1×10^{-2}. Some of the larger samples contained added HCl. However, with C_{Fe} less than 4×10^{-5} mol L^{-1} and C_{HCl} greater than 2×10^{-5} mol L^{-1} the saturated vapor absorbances fell in group C. When a large fraction of the $FeCl_2$ in a group A sample with HCl present was sealed off in the tip after the HCl was condensed in the cell, the remaining material gave absorbances falling in group C. For group C samples, C_{HCl} ranged between 2×10^{-5} and 1.2×10^{-3} mol L^{-1} with no systematic dependence of absorbances on C_{HCl}. We speculate that the total free energy of the crystallites is increased by adsorption of HCl or that the crystal structure is modified. The two groups of points appear to be converging at higher temperatures but seem clearly separated at lower temperatures. Shifts from one group to the other were not observed as breakover points were approached, i.e., as the last trace of solid vaporized. For both groups absorbances could be retraced on heating and cooling. A relatively high HCl:$FeCl_2$ ratio appears necessary to stabilize the group C systems. Intermediate absorbances were observed when water was added (see below). The presence of water may lead to formation of hydroxyhalide vapor molecules which could add to the absorbance; however, no systematic dependence of the added absorbance to C_{HCl} and/or C_{H_2O} was established.

A least-squares analysis of 60 data points from the five samples represented in group C gave the equation $\ln(A_{241}T/b) = (-21\,400 \pm 200)T_3^{-1} + (28.8 \pm 0.2)$. If compared with JANAF thermodynamic data[3] with E_M assumed to be 4700 M^{-1} cm^{-1}, this result corresponds to $\Delta G° = 2600 - 2.5T$ for the change $FeCl_2$(s, JANAF) = $FeCl_2$(s, Group C).

Interaction of Iron(II) Chloride with Quartz and Pyrex. When absorbances of samples containing unsaturated iron(II) chloride vapor were correlated with total amounts of iron in the cell, expressed as concentration equivalents, C_{Fe}, with the assumption of $C_{Fe} = C_M + 2C_D$, the JANAF equilibrium constant for reaction 2, and the equation given above for A/bC_M, the following differences were noted: (1) Molar absorptivities were obtained much lower than those derived above; (2) the absorbance increased more with increase in T than could be reasonably attributed to increased dissociation of dimer; (3) at lower temperatures the absorbance was reproducibly dependent on T_3 even though no solid or liquid $FeCl_2$ was believed present in the tip; (4) the absorbance decreased slowly and variably with time and more rapidly the higher the temperature (a decrease of about 1% h^{-1} at 640 °C, for example). Observations 1, 2, and 4 indicate that iron(II) chloride reacts with quartz, forming nonvolatile but soluble iron complexes on or near the surface. Except for the small decrease with time, the reproducible variation of absorbance with temperature, observation 2, indicates that the interaction is reversible. Additional evidence is discussed below.

Formation of HCl in a 10-cm cell containing a relatively large amount of $FeCl_2$ ($C_{Fe} = 4.1 \times 10^{-3}$) was observed in the following experiment. A sample, containing only $FeCl_2$ prepared from iron wire and chlorine in a quartz system, was heated quickly to 600 °C, held there for 15 min, and cooled rapidly to room temperature. Vapor absorbance at 190 nm indicated HCl present with C_{HCl} at 3.3×10^{-5} mol L^{-1}. The gas, which condensed with liquid nitrogen but not dry ice, as expected for HCl, was frozen in the tip and sealed off. The sample was then heated to 405 °C and held there for 2.5 h, after which no HCl was detected. Additional heating at 640 °C for 1.5 h produced an HCl concentration of 1.4×10^{-5} mol L^{-1}. With the excess of $FeCl_2(s)$ in the cell the saturated vapor absorbance ($FeCl_2$) did not change with time or depend on the HCl concentration. The HCl is presumed to have formed by interaction of $FeCl_2$ with hydroxo groups or tightly bound water in or on the surface of the quartz,[10,11] even though every effort was made to dry the cell by strong preheating under vacuum before $FeCl_2$ was added. The OH groups in commercial fused quartz are reported to range from 3×10^{-4} to 0.12% by weight, depending on the method of preparation,[10] and at high temperatures reactive siloxane type sites are said to be available.[12] IR studies of the reaction of various chlorinated species (not iron halides) with such sites have been reported.[11,12,13]

Data for several unsaturated iron(II) chloride vapor samples prepared in all-quartz systems are shown in Table I. These samples exhibited behaviors 1 and 4; so that the interaction with the cell could be minimized, only a few absorbances were measured in each case. Except for sample 3, $FeCl_2$ was flame sublimed into the cell body prior to analysis; yet detectable amounts of iron remained in the side arm. The amount of this "residual" iron (i.e., iron not transferred by flaming) is significantly less than the amount of iron not contributing as $FeCl_2$ to the absorbance. The "missing" iron was presumably condensed although it could have been in a volatile but nonabsorbing form. If it is condensed, the reaction that forms

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(10) L. Holland, "The Properties of Glass Surfaces", Wiley, New York, 1964, p 223 f and references therein.

(11) H.-P. Boehm, M. Schneider, and F. Arendt, *Z. Anorg. Allg. Chem.*, **320**, 43 (1963).

(12) B. A. Morrow and I. A. Cody, *J. Phys. Chem.*, **79**, 761 (1975).

(13) R. Tubis, B. Hamlett, R. Lester, C. G. Newman, and M. A. Ring., *Inorg. Chem.*, **18**, 3275 (1979) and references therein; M. L. Hair and W. Hertl, *J. Phys. Chem.*, **77**, 2070 (1973).

it must be at least partially reversible as some of the iron is removed when the cell is flamed. Amounts of both "condensed" and "residual" iron are lower when the heating time is shorter and C_{HCl} is higher. Sample 6 gives the highest molar absorptivity, approaching the value derived from saturated vapor absorbances and JANAF thermodynamic constants. It is concluded that the reaction of $FeCl_2$ with quartz is at least partially reversible and the extent of reaction is reduced by increasing the concentration of HCl and decreasing the period of heating.

When iron(II) chloride had been sublimed in Pyrex, other complications arose which are explained if a small fraction of $FeCl_2$ reacts with sodium oxide in the Pyrex[14] to form Na_2FeCl_4 and FeO. When a relatively large amount of $FeCl_2$ was flame sublimed back and forth several times (~550–650 °C) in an evacuated Pyrex tube (30 cm long, 0.5 cm i.d.) it was found that a white solid, melting at 367–379 °C to a colorless liquid, could be separated from the $FeCl_2$. The presence of gas with volatility characteristics of HCl was also noted. NaCl and $FeCl_2$ are reported to form Na_2FeCl_4, which melts incongruently at 400 °C with a eutectic mixture (44 mol % $FeCl_2$) melting at 374 °C.[15] Flame photometric analysis showed an abundance of sodium in a sample of the white solid. Observations to follow indicate that some of the adduct was transported into the cells when $FeCl_2$ was sublimed and that the presence of the adduct in the cells accounts for observation 3 above.

Vapor absorbances above solid $FeCl_2$ prepared in Pyrex–quartz systems agree well with those from samples prepared in quartz (see group A, Figure 1) with no indication of detectable contributions from gaseous complexes such as $NaFeCl_3$.[16] However, after complete vaporization of the solid (above the breakover point) the absorbance for the Pyrex–quartz samples (seven were studied) still increased slightly as T and/or T_3 was increased. The T_3 dependence was not observed with samples prepared in quartz. A particularly well-characterized example is shown in Figure 1 as points in group B; HCl had been added to this sample. The T_3 dependence above the breakover point probably reflects vaporization of $FeCl_2$ from a small amount of Na_2FeCl_4. In the T-dependent region, the slight additional increase is more than expected from dimer dissociation or formation of $NaFeCl_3(g)$[16] and is attributed to the HCl–nonvolatile-iron interaction mentioned previously. At the highest temperature the absorbance decreased only 2% in 50 h demonstrating the stabilizing effect of HCl. After cooling, the $FeCl_2$ was flame sublimed into the cell from the side arm; analysis gave C_{Fe}(cell body) = 1.09×10^{-5} mol L^{-1}, C_{Fe}(side arm) = 5.7×10^{-7} mol L^{-1}, C_{Na}(cell body) = 0, C_{Na}(side arm) = 5.4×10^{-7} mol L^{-1}, and C_{HCl} (added) = 1.2×10^{-3} mol L^{-1}. For the unsaturated vapor at 650 °C, $A_{241}/bC_{Fe(total)}$, the apparent molar absorptivity, was 3930 M^{-1} cm^{-1}, showing the effect of the relatively high concentration of HCl. Amounts of sodium and iron in the side arm are similar and small compared with the total amount of iron in the cell.

Observations with mixtures of $FeCl_2$ and $FeCl_3$ also indicated interaction with Pyrex. After mixtures with mole ratios $FeCl_2$:$FeCl_3$ from 0.043 to 2.1 that had been prepared in Pyrex–quartz were cooled, trace amounts of a reddish yellow film were observed along with white and black crystals of $FeCl_2$ and $FeCl_3$, respectively. When it was heated, the film melted below 250 °C (amounts were too small to determine the melting point accurately) and iron(III) chloride vaporized out of the liquid, leaving a white deposit. The film is believed to be $NaFeCl_4$ (mp 163 °C),[17] possibly formed by the reaction

$$2FeCl_3 + Na_2FeCl_4 = 2NaFeCl_4 + FeCl_2 \qquad (3)$$

and may also include dissolved $FeCl_2$ (the $FeCl_2$–$FeCl_3$–NaCl system shows a considerable range of mutual solubility).[18] In comparison with earlier work[1] the vapor-phase absorbances indicated only the presence of $FeCl_3(g)$, $Fe_2Cl_6(g)$, and $NaFeCl_4(g)$. The presence of sodium was confirmed by flame photometry; in one case the amount was as large as 10 mol % of the total amount of iron.

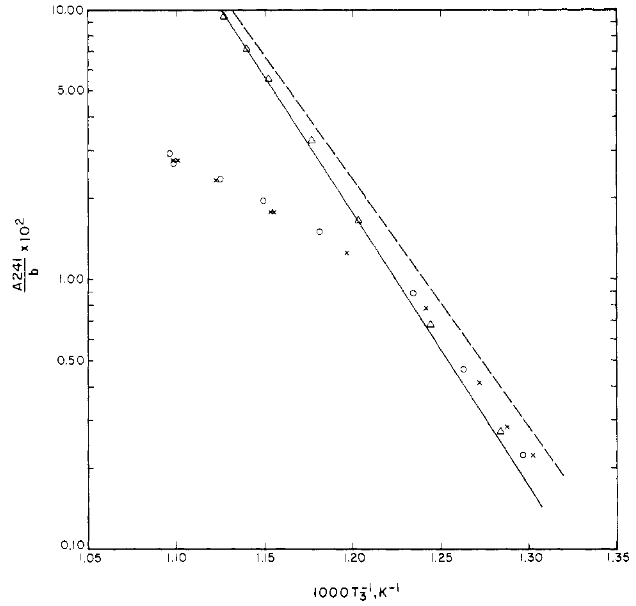

Figure 2. Temperature dependence of absorbance at 241 nm of iron(II) chloride samples to which HCl, H_2O, and H_2 were added (see text): (×) sample I; (○) sample II; (△) sample III; (—) least-squares line for group A points, Figure 1; (- - -) least-squares line for group C points, Figure 1. Temperature range for the vapor was 915–958 K.

For a better assessment of the role of water in the behavior of the various samples, measured amounts, along with HCl and in two cases H_2, were added to three samples of $FeCl_2$ prepared in quartz. Cells used were 10 cm long with volume ca. 30 cm^3. The concentration equivalents 10^3C_{HCl}, $10^3C_{H_2O}$, $10^3C_{H_2}$, 10^5C_{Fe}(cell body), and 10^5C_{Fe}(side arm) were as follows, respectively: sample I, 1.31, 1.08, 0.0, 0.130, 2.86; sample II, 1.26, 1.03, 0.98, 0.0, 3.12; sample III, 1.85, 1.02, 1.27, 0.330, 2.38. Quantities of iron were determined following absorbance measurements which are shown in Figure 2. With samples I and II the following was observed: (1) Windows and the tip of the side arm became etched, a behavior not observed in samples to which water had not been added. While the presence of water seems to be the principal cause of etching, the problem was exacerbated by the long heating periods (1–2 days at 650 °C) necessary to sublime $FeCl_2$ into the tip with the moderately high total gas pressures in the cell. White etched spots, which appeared to be covered with small crystals found insoluble in HNO_3, were observed on the windows where part of the solid $FeCl_2$ first deposited before finally collecting in the tip. (2) Absorbances varied with T_3 throughout the range studied (see Figure 2). (3) After the cell was cooled and volatile gases were condensed in the cell body with liquid nitrogen, flaming the tip resulted in sublimation of larger amounts of $FeCl_2$ than expected from the

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(14) Corning Pyrex Brand, Code 7740, contains the following: SiO_2, 81%; Al_2O_3, 2%; Na_2O, 4%; K_2O, 0.5%; B_2O_3, 13%; others, 0.05–0.5% (Corning Laboratory Products Catalog, 1971).

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highest absorbances observed. (4) Only white deposits were observed. (5) Absorbances increased with T_3 along the $FeCl_2(s)$ saturation line to a point about double the absorbance at the apparent breakover point (Figure 2), but when the sample was held at these temperatures for some time, the absorbance slowly decreased to the values shown (Figure 2) and could then be reproduced on heating and cooling. After the sample was cooled below the breakover point, behavior 5 was observed again.

Etching was not observed with sample III. Saturated absorbances close to those of the group A samples (Figure 1) were observed up to the breakover point (622 °C, not in the range of Figure 2). At higher temperatures the absorbance increased only slightly as T_1 was increased and was independent of T_3. At 719 °C, $A_{241}/bC_{\mathrm{Fe(total)}}$ was 3790 M^{-1} cm^{-1}. Water had no particular effect on this sample; the apparent molar absorptivity, with C_{HCl} relatively high, approaches that derived from JANAF data earlier, as expected from the behavior of the samples in Table I.

Equilibrium constants for reaction 4[3,19,20] indicate, for the

$$FeCl_2(s) + {}^1/_2SiO_2(s) + H_2O(g) = {}^1/_2Fe_2SiO_4(s) + 2HCl(g) \quad (4)$$

amounts of HCl and H_2O in samples I and II, respectively, that the $FeCl_2$ solid phase should disappear at ca. 570 °C. The temperature indicated by data in Figure 2, 544 °C, is somewhat lower; however, on first heating a breakover point around 575 °C was observed (see behavior 5 above), after which absorbances fell to the range shown in Figure 2. This may indicate a change in the composition of the silicate phase. In sample III the HCl:H_2O ratio is larger and the $Fe_2SiO_4(s)$ phase is not predicted to be stable below ca. 619 °C, which accounts for the lack of etching and the independence from variations in T_3 of the high-temperature absorbances.

The qualitative observations 1–5 and the calculations based on reaction 4 are consistent with the conclusion that iron(II) chloride reversibly reacts with quartz in the presence of water. However, because of the limited (trace?) amounts of water present in the samples to which water was not added, the Fe–O–Si phase formed may differ from the phase for which thermodynamic properties are given. Values of $K = P_{\mathrm{FeCl_2}} \cdot (P_{\mathrm{H_2O}}/P_{\mathrm{HCl}}{}^2)$ for reaction 5 were derived from the absorbances

$$ {}^1/_2Fe_2SiO_4(s) + 2HCl(g) = FeCl_2(g) + {}^1/_2SiO_2(s) + H_2O(g) \quad (5)$$

(with the assumption $E_M = 4700\ M^{-1}\ cm^{-1}$) of samples I and II above the breakover point (Figure 2). A least-squares treatment of ln K vs. $1/T_3$ led to $\Delta H° = 15.7 \pm 0.6$ kcal (mol of $FeCl_2)^{-1}$ and $\Delta S° = 6.2 \pm 0.1$ cal deg^{-1}, with predicted[3,20] values of 18.7 kcal mol^{-1} and 11.4 cal deg^{-1}, respectively. It is not unlikely that the condensed phase may be a solution of varying composition or involve other species.

Absorbances below the breakover points for samples I and II lie between the group A and C lines. Addition of substantial amounts of water decreases the effect of HCl on the absorbance in the saturated vapor range. The addition of hydrogen to samples II and III had no discernable effect, suggesting that iron(III) oxide is not involved in the reaction controlling the absorbance. Iron(III) oxide would be reduced at the concentration of hydrogen present;[3] iron(III) silicate is unstable.[19]

Iron(II) Chloride–Iron(III) Chloride Mixtures. Absorbances of vapors generated by a number of mixtures of $FeCl_2$ and $FeCl_3$ were examined for irregularities which might indicate contributions from mixed-valence-state molecules. Samples prepared in Pyrex were found to contain small amounts of $NaFeCl_4$, as discussed above, which complicated the interpretation. A sample prepared in quartz by photolysis of $FeCl_3$[5] did not present these difficulties and was examined between 180 and 630 °C. The composition, after removal of chlorine, was $C_{\mathrm{FeCl_3}} = 6.93 \times 10^{-5}$ mol L^{-1} and $C_{\mathrm{FeCl_2}} = 14.4 \times 10^{-4}$ mol L^{-1}. A slight reaction of the unsaturated vapor with quartz (absorbance decreased very slowly with time) could be seen at the highest temperature. The spectra correlated with behavior expected for a mixture of $FeCl_3(g)$, $Fe_2Cl_6(g)$, and $FeCl_2(g)$. Fe_3Cl_8 has been detected in a mass spectrometric study,[21] but thermodynamic properties of this molecule are not known. If its properties relative to those of $FeCl_3$ and $FeCl_2$ are similar to those of other $M^{II}M^{III}{}_2X_8$ species,[22,23] its maximum mole fraction in this mixture would be only of the order of 0.04 and its contribution to the total absorbance observable only if it has a high molar absorptivity in a region of the spectrum where the major species do not absorb. Spectrophotometric data were examined between 200 and 2200 nm (to include a region where d–d transitions might be observed) with no evidence seen for the presence of Fe_3Cl_8.

A comparison of molar absorptivities calculated from saturated vapor absorbances of $FeCl_3(g)$ and $Fe_2Cl_6(g)$ and JANAF thermodynamic data[3] with those based on unsaturated vapor[1] and the total amount of iron present shows discrepancies similar to those described for $FeCl_2(g)$ in the present work. This was also noticed in an earlier study.[24] If some of the iron in the $FeCl_3$ system, also in the presence of excess chlorine, is converted to a nonabsorbing (but soluble) form, values for the molar absorptivities based on the unsaturated vapor absorbances may be too low. We intend to reexamine this question. The conclusion reached above concerning Fe_3Cl_8 would not be affected by this uncertainty.

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