

Figure 6. Shake-up spectrum of the Xe 3d orbital in XeF₆. Counts on the Xe 3d_{5/2} line total over 3000. The lines are a seven-point smooth to the data.

energy of the lowest unoccupied molecular orbital ($8e_u^*$). The monopole selection rules allow transitions to this virtual level from the $7e_u$, $6e_u$, or $5e_u$ valence orbitals. Since only the $6e_u$ valence orbital has appreciable Xe character, we would predict the transition to be $6e_u \rightarrow 8e_u^*$. With the eigenvalues obtained from the DVM- $X\alpha$ calculation, the transition energy is 10.2 eV, which corresponds almost exactly with that observed for peak 1 (10.7 eV). This transition ($6e_u \rightarrow 8e_u^*$) is analogous to the lowest energy shake-up peak observed in XeF₂ ($6\sigma_u \rightarrow 7\sigma_u^*$).

In lieu of a theoretical calculation dealing with the higher virtual levels in XeF₄, we have used the atomic model to assign peaks 2 and 3. The Rydberg 6s and 6p orbitals of XeF₄ are positioned exactly as they were in XeF₂.³ The two orbitals containing the majority of the Xe 5p character are the $4a_{2u}$

and the $5a_{2u}$ levels. The energies of the two shake-up transitions ($5a_{2u} \rightarrow 6p$; $4a_{2u} \rightarrow 6p$) can be easily determined via the atomic model in conjunction with the experimental valence binding energies.²¹ As is evident in Table VII, the calculated $4a_{2u} \rightarrow 6p$ transition at 22.3 eV is much closer to the observed (21.8 eV) than the $5a_{2u} \rightarrow 6p$ transition (17.5 eV).

Peak 3 has been assigned to the $9a_{1g} \rightarrow 6s$ transition. The $9a_{1g}$ orbital is 74.5% Xe s in character. Hence this shake-up transition is analogous to the atomic Xe $5s \rightarrow 6s$ transition. The agreement here is the poorest as one might expect since the atomic model assumes that the Xe 5s orbital shifts the same amount as the predominantly Xe 5p orbitals on core hole formation.

The Xe 3d shake-up spectrum of XeF₆ is presented in Figure 6. It was not possible to obtain a reasonable Xe 4d spectrum because of channeltron degradation. We did not attempt a computer fit of this spectrum because of its complexity and lack of resolution. As with XeF₂ and XeF₄, there is one clearly defined low-energy peak corresponding to the first bonding to antibonding transition. The shake-up peak associated with the Xe 3d_{3/2} level has been assigned on the spectrum. The analogous peak resulting from Xe 3d_{5/2} ionization is hidden beneath the F 1s peak. A recent DVM- $X\alpha$ calculation on XeF₆²⁰ has located the lowest unoccupied molecular orbital ($8t_{1u}^*$). Monopole selection rules allow transitions from the $5t_{1u}$, $6t_{1u}$, and $7t_{1u}$ valence orbitals. An investigation of the orbital character from our $X\alpha$ -SW calculation²² shows that of these three orbitals, only the $6t_{1u}$ has significant Xe p character (28.8%). The excitation energy calculated for the $6t_{1u} \rightarrow 8t_{1u}^*$ transition by using both SW- $X\alpha$ ²³ and DVM- $X\alpha$ ²⁰ calculations is 11.8 eV.

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Thermodynamic Properties of Iron(III) Oxychloride

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Vapor-phase concentrations of Fe₂Cl₆(g) above solid mixtures, formed by interaction of Fe₂O₃ and FeCl₃, have been measured spectrophotometrically in the range 465–560 K. The equilibrium behavior, assumed to characterize the reaction $6\text{FeOCl}(s) = 2\text{Fe}_2\text{O}_3(s) + \text{Fe}_2\text{Cl}_6(g)$, projects pressures at higher temperatures which, within experimental uncertainty, agree with manometric data obtained with a Pyrex diaphragm gauge (580–670 K) and with earlier manometric measurements (660–770 K) reported by Stirnemann. A least-squares treatment of the combined absorbance and manometric data, using an estimated equation for ΔC_p° , gives the following relationship: $\ln P_{\text{Fe}_2\text{Cl}_6(\text{atm})} = -12.89 \ln T + 0.01755T - 5.827 \times 10^{-6}T^2 - 18550T^{-1} + 101.59$. Pressures given by this equation are substantially higher than those predicted for this reaction from thermodynamic constants reported by others. Possible reasons for the discrepancy are discussed.

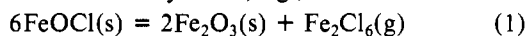
In a recent paper Stuve, Ferrante, Richardson, and Brown¹ report heat capacity data for FeCl₃(s) (4.6–300 K) and for FeOCl(s) (6–700 K) and a value for the standard enthalpy of formation of FeOCl(s) at 25 °C. The last value is based on measured heats of solution of FeOCl(s) in aqueous HCl

and heats of solution and the standard enthalpy of formation of FeCl₃(s).^{2,3} Standard thermodynamic constants are tabulated for FeOCl(s) at various temperatures. When used together with thermodynamic constants reported in ref 3 for

(1) Stuve, J. M.; Ferrante, M. J.; Richardson, D. W.; Brown, R. R. *Rep. Invest.—U.S., Bur. Mines* **1980**, RI-8420.

(2) See also: Schafer, H.; Wittig, F. E.; Jori, M. *Z. Anorg. Allg. Chem.* **1956**, **287**, 61.
(3) "JANAF Thermochemical Tables", Supplement; Dow Chemical Co.: Midland, MI, June 30, 1965.

$\text{Fe}_2\text{O}_3(\text{s})$ and $\text{Fe}_2\text{Cl}_6(\text{g})$, equilibrium pressures predicted for reaction 1 are substantially lower, e.g., factors of 16 around



750 K and 40 around 600 K, than observed by Stirnemann.⁴ In the present study mixtures of Fe_2O_3 and FeCl_3 have been equilibrated between 465 and 560 K and the vapor-phase concentrations of Fe_2Cl_6 determined from measured absorbances at 360 nm. Total pressures of the vapor developed by such mixtures have also been measured between 580 and 670 K in a Pyrex diaphragm gauge. Results of both studies are in general agreement with those of Stirnemann. Thermodynamic constants are derived from the equilibrium data, and differences from current literature values are discussed.

Experimental Section

Vapor-phase absorbances were measured with a Cary 14H spectrophotometer.⁵ A Pyrex side arm, 5–10 cm in length, was attached to the center of each of the cylindrical quartz absorption cells. A weighed sample of Fe_2O_3 (Baker Analyzed reagent) was transferred to the tip of the side arm, which was also attached to a Pyrex assembly containing a weighed piece of iron wire (Baker and Adamson Standardization iron wire) and, in a separate tube, $\text{CuCl}_2(\text{s})$. After the apparatus was flamed under high vacuum, chlorine, released by heating the CuCl_2 , was trapped in a connecting U-tube. The system was then closed off from the vacuum pumps and the chlorine allowed to vaporize; the iron was heated and completely converted to FeCl_3 . The FeCl_3 was then sublimed, in a small partial pressure of chlorine, into the main cell side arm. After cooling, the cell was evacuated and sealed off. Four mixtures were prepared.

sample	mol of $\text{Fe}_2\text{O}_3 \times 10^4$	mol of $\text{Fe} \times 10^4$	cell path length, cm	cell vol. cm^3
1	2.64	1.72	2	8.0
2	6.44	3.22	10	30.0
3	6.25	1.93	10	30.0
4	6.25	0.892	2	8.0

Cell temperatures were measured with chromel–alumel thermocouples that were calibrated at the boiling point of water and the melting point of tin. The cell center was kept between 10 °C (2-cm cells) and 20 °C (10-cm cells) above the temperature of the solid phases in the side-arm tip to ensure that deposits did not form on the windows, which were then a few degrees above the tip. Rather long times at fixed temperatures were required for equilibration. Several days to 1 week was needed for sample 1; the other samples had larger excesses of Fe_2O_3 and in these cases 24 h was generally found sufficient. Absorbances were accepted as equilibrium values when no change was observed on successive days and when values observed in a series of progressively increased temperatures agreed with those observed in a series of progressively decreased temperatures.

In the visible region of the spectrum, measurement of the absorbance of Fe_2Cl_6 vapor between 450 and 550 K is complicated by photolysis.⁶ To avoid significant error from this reaction, the spectrophotometer was set at 360 nm and the absorbance measured in the few seconds needed to make certain that the instrument had stabilized. The selected wavelength is virtually at the absorption peak maximum in this range (360–365 nm); hence, the absorbance, while high, is relatively insensitive to small variations in the wavelength setting. This initial reading, taken as the correct value, was followed by a recording scan at 1 nm s^{-1} from 380 to 340 nm to observe the shape of the spectrum in the vicinity of the maximum, after which the absorbance at 360 nm was measured again. Typically, a reduction of the order of a few percent was seen after the 40-s exposure. Equilibrium concentrations were reestablished during the “dark” equilibration periods. Each time the absorbance was also measured at 600 nm to verify the base-line position.

For manometric measurements a Pyrex thin-walled diaphragm gauge, volume ca. 30 cm^3 , with null point detected by motion of a thin rod sealed to the diaphragm, was constructed. Fe_2O_3 ($32.5 \times$

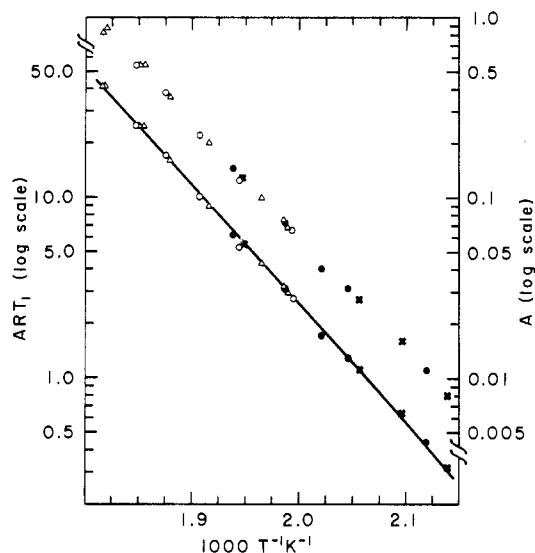


Figure 1. Plots of A (ordinate scale on right) and $(ART)_1$ (ordinate scale on left) vs. $1/T_3$ for vapor in equilibrium with various mixtures. A is the observed absorbance divided by the path length. Sample numbers, initial $n_{\text{Fe}_2\text{O}_3}/n_{\text{FeCl}_3}$ ratios, and symbols: 1, 1.54, Δ ; 2, 2.00, \bullet ; 3, 3.23, \times ; 4, 7.01, \square . The solid curve corresponds to the least-squares solution: $Y = \ln (ART)_1 + 12.89 \ln T_3 - 0.01755T_3 + 5.827 \times 10^{-6}T_3^2 = -18582T_3^{-1} + 110.89$.

10^{-4} mol) and FeCl_3 (7.08×10^{-4} mol), prepared as described for the absorbance samples, were introduced. The gauge was evacuated and sealed by collapsing the connecting side arm. Internal pressures, which developed as the sample was heated, were balanced by adjusting the pressure of air admitted on the opposite side of the diaphragm. Air pressures were measured with a mercury manometer; the diaphragm sensitivity was ± 0.5 torr. Temperatures at the top and middle of the gauge were kept ca. 10 °C above the temperature of the solid mixture at the bottom. The bottom temperature was used as the equilibrium temperature for correlation of the data.

The approach to equilibrium in the manometric experiments was also very slow, particularly as temperatures were lowered sequentially. Even 1 week after lowering the temperature to a set value, the observed pressure was still falling slowly. A possible explanation is that particles of Fe_2O_3 become coated with FeOCl , which inhibits reaction of underlying material with the vapor. The pressures assumed to represent equilibrium values were measured in a sequence of progressively increased temperatures after the mixture had been preheated to 410 °C, at which all the iron(III) chloride was in the vapor phase, and cooled. Pressures were observed daily at a given temperature for periods of several days to 1 week. A slow approach to equilibrium was also reported by Stirnemann.⁴

Results and Discussion

Vapor-phase absorbances at 360 nm, observed at various temperatures, are shown graphically in Figure 1. Results from the four independent samples, with substantially different $n_{\text{Fe}_2\text{O}_3}/n_{\text{FeCl}_3}$ ratios, are seen to correlate well, from which one concludes that the vapor concentration is controlled by the same equilibrium reaction in each case. Comparison of the spectrum between 230 and 600 nm with earlier work⁷ indicated that the dominant absorbing species was $\text{Fe}_2\text{Cl}_6(\text{g})$. Partial pressures of Fe_2Cl_6 , taken as equilibrium constants for reaction 1, were derived from the two equations $ART = E_M P_M + E_D P_D$ and $K_D = P_D/P_M^2 = \exp(17385T^{-1} - 17.082)$. A represents the absorbance, $R = 0.08206 \text{ L atm mol}^{-1} \text{ deg}^{-1}$, T is the vapor temperature (cell body), E_M and E_D are the molar absorptivities of monomer ($\text{FeCl}_3(\text{g})$) and dimer ($\text{Fe}_2\text{Cl}_6(\text{g})$), respectively, and P_M and P_D are the corresponding partial pressures. The constants in the equation for K_D , the equilibrium constant for the reaction $2\text{FeCl}_3(\text{g}) = \text{Fe}_2\text{Cl}_6(\text{g})$, were derived from data at 500 K, as given in ref 3. E_M was taken

(4) Stirnemann, E. *Neues Jahrb. Mineral., Geol. Palaeontol., Beilage, Abt. A* **1925**, 52, 334.

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Table I

data source	no. of observns	treat-ment	$\Delta H^*{}^a$	$\Delta S^*{}^b$	at 500 K				
					ΔH°	ΔS°	$S^\circ(\text{FeOCl}(s))$	Δ	Δ'
Thermodynamic Constants Based on Equilibrium Data for Reaction 1 ^c									
abs	23	i	37 275 (0.57) ^d	202.66 (0.21)	30 293	44.08	29.57	1574	1202
		ii	38 683 (0.27)	205.62	31 701	47.04	29.02	1222	850
		iii	38 856 (0.29)	205.95	31 874	47.36	29.02	1179	807
diaphragm gauge	12	i	37 998 (2.50)	203.64 (0.74)	31 015	45.06	29.40	1394	1021
		ii	39 226 (0.39)	205.62	32 244	47.04	29.02	1087	714
		iii	39 438 (0.39)	205.95	32 456	47.36	29.02	1034	661
Stirnemann ⁴	25	i	34 689 (0.41)	198.83 (0.10)	27 706	40.25	30.21	2221	1849
		ii	39 532 (0.67)	205.62	32 550	47.04	29.02	1010	638
		iii	39 774 (0.70)	205.95	32 792	47.36	29.02	950	577
all data	60	i	36 859 (0.22)	201.85 (0.07)	29 876	43.27	29.70	1679	1306
		ii	39 146 (1.10)	205.62	32 163	47.04	29.02	1107	734
		iii	39 355 (1.17)	205.95	32 373	47.36	29.02	1054	682
predicted, ref 1 and 3					36 588	47.04	29.02		
Thermodynamic Constants from Van't Hoff Treatment of Absorbance Data with ln (ART) in Place of ln P _D									
reacn 1	23		36 922 (0.57)	220.34 (0.19) ^e	29 939	61.76 ^e			
reacn 2	49		25 464 (0.71)	-250.94 (0.16) ^e	31 997	73.63 ^{e,f}			
reacn 3 ^g			-5 729	-235.64	1 029	5.94	29.95		1480

^a All enthalpy values given in cal mol⁻¹. ^b All entropy values given in cal mol⁻¹ deg⁻¹. ^c (i) Van't Hoff treatment. (ii) Third law treatment with ΔS^* fixed from the following values of $S^\circ(500 \text{ K})$: FeOCl(s), 29.02;¹ Fe₂O₃(s), 35.47;³ Fe₂Cl₆(g), 150.22.³ (iii) Same as (ii) but with $S^\circ(500 \text{ K})$ of Fe₂Cl₆(g) as 150.54.⁷ ^d Standard deviation (%) shown in parentheses. ^e $\Delta S + R \ln E_D$. ^f From data in ref 7. ^g From the two preceding sets of results for reactions 1 and 2.

as 5800 and E_D as $14011 - 7T \text{ M}^{-1} \text{ cm}^{-1}$.⁷ The contribution of the monomer to the absorbance is predicted to be very small; calculated P_M/P_D ratios for the absorbance samples were of the order of 10^{-2} .

Total pressures observed manometrically were assumed to represent the sum $P_D + P_M + P_{\text{Cl}_2}$, with relative partial pressures fixed by the two equilibrium reactions $2\text{FeCl}_3(\text{g}) = \text{Fe}_2\text{Cl}_6(\text{g}) = 2\text{FeCl}_2(\text{s}) + \text{Cl}_2(\text{g})$. The equation $K_{\text{Cl}_2} = P_{\text{Cl}_2}/P_M^2 = \exp(20497T^{-1} - 25.450)$, derived from data at 500 K in ref 3, together with K_D and P_{total} , was used to derive the separate partial pressures. The contribution of chlorine is also small; calculated ratios P_{Cl_2}/P_D for the manometric samples were between 0.048 (584 K) and 0.013 (777 K).

Data were correlated by using the equation $\Delta C_p^\circ = -25.61 + 0.06975T - 6.95 \times 10^{-5}T^2 \text{ cal mol}^{-1} \text{ deg}^{-1}$ for reaction 1. The given constants were fixed from values of ΔC_p° at 500, 600, and 700 K as -8.11, -8.78, and -10.84 cal mol⁻¹ deg⁻¹, respectively, based on data for Fe₂O₃ and Fe₂Cl₆ in ref 3 and for FeOCl as given in ref 1. This leads to the expression $Y = \ln P_D + 12.89 \ln T - 0.01755T + 5.829 \times 10^{-6}T^2 = -\Delta H^*/RT + \Delta S^*/R$

A linear least-squares treatment, Y vs. $1/T$, was used to derive values of the enthalpy- and entropy-related constants, ΔH^* and ΔS^* . Results, with standard deviations and values of ΔH_1° and ΔS_1° at 500 K, obtained from the independent and combined sets of data, are listed in Table I.

When extended to the temperature range of the manometric measurements, the least-squares equation for P_D generated by the absorbance data predicts the pressures shown as a line in Figure 2. The agreement is quite good for the diaphragm gauge results and with the lower range of Stirnemann's observations.⁴ The projected pressures at the upper range of Stirnemann's data are high, and a better overall fit for all observations is given by the least-squares treatment of the combined sets of data (see Table I) as shown by the solid line, which also fits well for the absorbance data in its range.

As shown in Figure 2, the equilibrium pressures predicted for reaction 1 from data in ref 1 and 3 lie well below the observed values. These values were calculated by using free energy functions and the value of ΔH°_{298} for FeOCl(s) from ref 1 and similar values for Fe₂O₃(s) and Fe₂Cl₆(g) from ref 3. Corresponding values of ΔH_1° and ΔS_1° at 500 K are

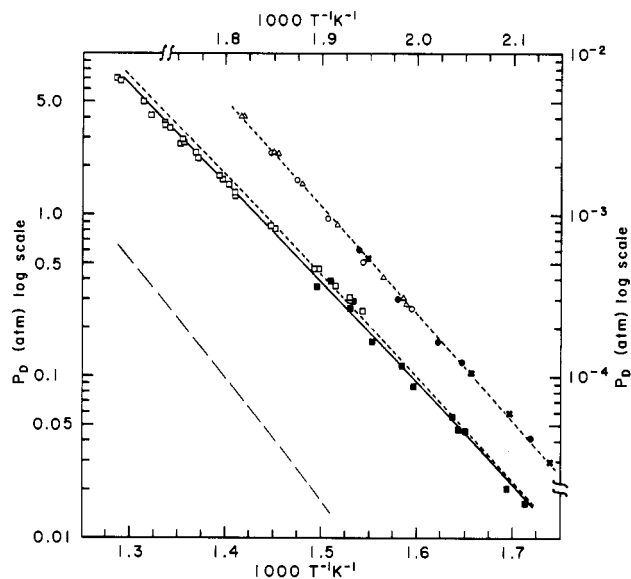


Figure 2. Plots of P_D (log scale) vs. $1/T$. Data based on lower abscissa and left ordinate scales: Stirnemann, \square ; this work, diaphragm gauge, \blacksquare ; least-squares curve using all 60 observations, —; least-squares curve based on absorbance data only, ---; curve predicted from data in ref 1 and 3, - - -. Data based on upper abscissa and right ordinate scales: absorbance data, symbols as identified in Figure 1 caption; least-squares curve based on absorbance data, ---.

shown in Table I; both are substantially higher than results given by any of the separate equilibrium data sets or by the combined set.

The enthalpy of formation of Fe₂Cl₆(g) is based on the enthalpy of sublimation and the enthalpy of formation of FeCl₃(s) and is assigned an uncertainty of $\pm 2 \text{ kcal mol}^{-1}$.³ In a recent vapor pressure study,⁸ a heat of sublimation ca. 1.5 kcal mol⁻¹ less than the previously adopted value is recommended; however, this change is insufficient to bring the ΔH_1° values into agreement. The enthalpy of formation of FeOCl(s) is based on a measurement of its heat of solution and the enthalpy of formation of FeCl₃(s). A small error from either of these sources will have its effect on the projected value of

(8) Rustad, D. S.; Gregory, N. W. *J. Chem. Eng. Data*, in press.

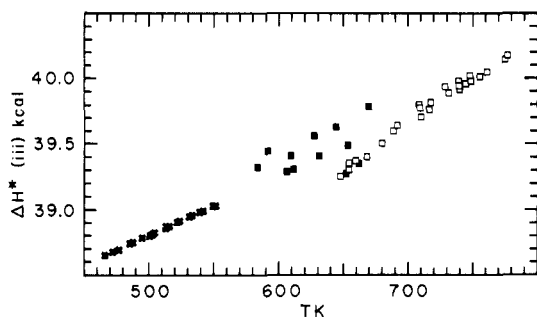


Figure 3. Variation of ΔH^* values (calculation iii; see Table I) with temperature: absorbance, \times ; diaphragm gauge, \square ; Stirnemann, \blacksquare .

ΔH_1° multiplied because of the involvement of 6 mol of FeOCl/mol of Fe_2Cl_6 in reaction 1. The quantities Δ and Δ' listed in Table I show, for example, the change that would be needed in $\Delta H^\circ(\text{FeCl}_3(\text{s}))$ to bring the predicted value of ΔH_1° into agreement with the value derived from the equilibrium data. The Δ values were calculated as follows:

$$\Delta H_1^\circ = \Delta H^\circ(\text{Fe}_2\text{Cl}_6) + 2\Delta H^\circ(\text{Fe}_2\text{O}_3) - 6\Delta H^\circ(\text{FeOCl})$$

With primary values from ref 1 and 3 at 500 K

$$\Delta H_1^\circ = (-155.57 + 2\Delta) + 2(-196.36) - 6(-97.48 + \Delta) = 36.59 - 4\Delta$$

or with the revised enthalpy of sublimation from ref 7

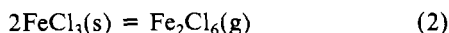
$$\Delta H_1^\circ = (-157.06 + 2\Delta') + 2(-196.36) - 6(-97.48 + \Delta') = 35.10 - 4\Delta'$$

The values of Δ derived (Table I) indicate that a somewhat smaller negative value is needed for $\Delta H^\circ(\text{FeCl}_3(\text{s}))$ than the $-95.46 \text{ kcal mol}^{-1}$ selected at 298 K in ref 3. Values as low as $-93.5 \text{ kcal mol}^{-1}$ have been reported.^{9,10} The corresponding change in ΔH° for Fe_2Cl_6 , with the revised heat of sublimation and the value of Δ of $1.4 \text{ kcal mol}^{-1}$, for example, would be within the uncertainty currently specific in ref 3.

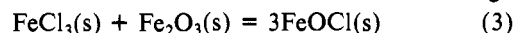
Values of ΔS_1° derived from the equilibrium data are also appreciably lower than predicted from ref 1 and 3. On the basis of an entropy or sublimation of $\text{Fe}_2\text{Cl}_6(\text{g})$ of $53.66 \text{ cal mol}^{-1} \text{ deg}^{-1}$,⁷ the revised value $S^\circ = 35.33 \text{ cal mol}^{-1} \text{ deg}^{-1}$ for $\text{FeCl}_3(\text{s})$ at 298 K,¹ and the estimate $S^\circ(500 \text{ K}) - S^\circ(298 \text{ K}) = 13.11 \text{ cal mol}^{-1} \text{ deg}^{-1}$ for $\text{FeCl}_3(\text{s})$,³ S° for $\text{Fe}_2\text{Cl}_6(\text{g})$ at 500 K is assigned the value $150.54 \text{ cal mol}^{-1} \text{ deg}^{-1}$. This is virtually the same as the $150.22 \text{ cal mol}^{-1} \text{ deg}^{-1}$ estimated in ref 3 by statistical thermodynamic methods. With S° for $\text{Fe}_2\text{O}_3(\text{s})$ at 500 K taken as $35.47 \text{ cal mol}^{-1} \text{ deg}^{-1}$,³ values of S° for FeOCl(s), derived from calculation i as $(150.54 + 2(35.47 - \Delta S_1^\circ))/6$, are listed in Table I. All are slightly higher (from 0.38 to $1.19 \text{ cal mol}^{-1} \text{ deg}^{-1}$) than the $29.02 \text{ cal mol}^{-1} \text{ deg}^{-1}$ given by the heat capacity study.¹

When the value of ΔS^* is selected so as to give the predicted (third law) result for ΔS_1° at 500 K, the enthalpy constants corresponding to results of treatments ii and iii, Table I, are obtained. They lead to values of ΔH_1° at 500 K somewhat closer to those predicted by ref 1 and 3 (still smaller by ca. 4 kcal) than those from the Van't Hoff treatment. However, as shown in Figure 3, the third law ΔH^* values increase systematically as the temperature increases and do not give a satisfactory correlation of the combined sets of data.

The entropy derived from the absorbance data is sensitive to the value selected for E_D . If one neglects the very small contribution to the absorbance from the monomer, the ratio of the absorbance of vapors for equilibrium 2 over the ab-



sorbance of vapors for equilibrium 1 leads to the values of the equilibrium constant for reaction 3 without the need to assign



a numerical value for E_D (the temperature dependence of E_D must also be neglected): $K_3 = (K_2/K_1)^{1/2} = ((P_D)_2/(P_D)_1)^{1/2} = ((ART/E_D)_2/(ART/E_D)_1)^{1/2} = (A_2/A_1)^{1/2}$. Constants derived by a least-squares treatment using $\ln(ART)$ in place of $\ln P_D$ are shown in Table I; the entropy constant now includes an unspecified contribution from E_D . A corresponding treatment of data from ref 7 gives

$$\ln(ART)_2 = 29.69 \ln T - 0.06472T + 1.85 \times 10^{-5}T^2 - 12814T^{-1} - 126.28$$

Subtracting the equation for $\ln(ART)_1$ leads to the enthalpy and entropy constants for reaction 3 shown in Table I. A value for $S^\circ(\text{FeOCl}(\text{s}))$ may now be calculated as $(\Delta S_3^\circ + 35.47 + 48.44)/3$ and of Δ' from $1029 = 3(-97.48 + \Delta') - (-94.15 + \Delta') - (-196.36)$. The results are similar to those based on pressures calculated by using the molar absorptivity. Hence, it does not appear that the uncertainty in the value of E_D has introduced an appreciable error.

It is possible that the calculated and observed behaviors differ because the FeOCl(s) phase generated in the equilibrium studies is not identical with that used for the heat capacity study and the heat of solution experiments. Recent papers describe the formation of intercalation complexes by FeOCl(s) and a number of amine bases, including ammonia.^{11,12} If a similar interaction between FeOCl and the chloride or oxide occurs to a significant degree in the equilibrium systems studied here, the thermodynamic properties of the FeOCl phase may be altered. However, the consistency of the data from the variety of samples studied (Stirnemann began with FeOCl; the starting $n_{\text{Fe}_2\text{O}_3}/n_{\text{FeCl}_3}$ ratios for the present absorbance samples varied from 1.5 to 7.0 and it was 4.6 for the diaphragm gauge sample; all the iron(III) chloride was driven into the vapor phase in the latter at the highest temperatures) would seem to require that the FeOCl(s) phase be the same in all cases. Nothing was seen to suggest involvement of a distinct phase intermediate between Fe_2O_3 and FeOCl, such as $\text{Fe}_3\text{O}_4\text{Cl}$.¹³ A room-temperature X-ray diffractometer powder study of the solid mixture removed from the diaphragm gauge after completion of the pressure measurements showed only lines expected from $\text{Fe}_2\text{O}_3(\text{s})$ and FeOCl(s).¹⁴ The Fe_2O_3 pattern was dominant, but diffractions from FeOCl hkl planes 010, 110, 111, 131, and 221 were well isolated and were observed at the angles predicted from the reported lattice constants.^{12,14} It is possible, of course, that the phase could be modified at the temperature of the equilibrium study.

A fifth absorbance sample, with oxide/chloride ratio 1/1, was held in the vicinity of 290 °C for 2 weeks, after which ca. 5% of the iron(III) chloride still remained unreacted in the vapor phase, a further example of the very slow uptake of ferric chloride when one attempts to convert all the Fe_2O_3 to FeOCl. Several other samples with very small amounts of FeCl_3 were studied. It was hoped that the absorbance could be followed as the last traces of FeCl_3 were driven into the vapor phase. For these samples the initial vapor absorbance did correspond with the amount of FeCl_3 introduced but the vapor concentration fell slowly with time, ultimately below the expected saturation limit, as though the $\text{Fe}_2\text{Cl}_6(\text{g})$ was dissolving in an unsaturated Fe_2O_3 -FeOCl mixture. A hysteresis-like behavior was observed on heating and cooling. Similar effects were not observed when relatively large amounts of FeCl_3 were used.

Registry No. Fe_2Cl_6 , 16480-60-7; FeOCl, 13870-10-5.

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